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⑯ Hair care compositions.

⑯ Hair care compositions which give both improved style retention and hair conditioning properties. The compositions comprise from about 0.01% to about 10% of a rigid silicone polymer and a volatile carrier.

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Description**HAIR CARE COMPOSITIONS****TECHNICAL FIELD**

5 The present invention relates to hair care compositions which have improved hair conditioning and style retention properties due to the inclusion of particular types of silicone polymers, and a volatile carrier for such polymers.

BACKGROUND OF THE INVENTION

10 The desire to have hair retain a particular shape is widely held. The two methodologies of accomplishing this are permanent chemical alteration of the hair or a temporary alteration. A temporary alteration is one which can be removed by water or by shampooing. This has generally been accomplished by means of the application of a separate composition to dampened hair, i.e., after shampooing and/or conditioning, and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousse, gels, lotions, and sprays. However, many people desire some improvement in style retention without the necessity of a separate step. Further, some people desire a high level of style retention such as that provided by a separate composition without the negative impact of these materials on dry hair properties, particularly ease of combing and hair feel.

15 Silicones in various hair care compositions have been disclosed in a large number of different publications, including U.S. Patent 3,964,500, Drakoff, issued June 22, 1976; U.S. Patent 4,364,837, Pader, issued December 21, 1981; U.S. Patent 4,341,799, Good, Issued July 27, 1982; U.S. Patent 4,465,619, Boskamp, issued August 14, 1984; U.S. Patent 4,515,784, Bogartus, issued May 7, 1985; U.S. Patent 4,387,090, Bolich, issued June 7, 1983; and U.S. Patent 4,529,586, DeMarco et al., issued July 16, 1985.

20 It has now been discovered that hair care compositions comprising certain rigid silicone polymers and volatile carriers provide increased style retention. The compositions may be in any of the conventional forms, including but not limited to shampoos, conditioners, hairsprays, tonics, lotions and mousse. The compositions provide the increased style retention to the hair without decreasing dry hair properties such as ease of combing.

25 This is surprising since other silicone materials which have been typically used in hair care compositions as conditioners have hurt style retention, and the resins and gums used frequently for style retention have generally hurt dry hair properties such as combing.

30 It is an object of the present invention to provide hair care compositions which contain a high molecular weight rigid silicone polymer.

35 It is a further object of the present invention to provide stable hair care compositions containing a volatile carrier.

It is a further object of the present invention to provide hair care compositions providing good style retention.

It is a further object of the present invention to provide hair care compositions which provide good conditioning.

40 It is a further object of the present invention to provide an improved method of temporarily styling and conditioning hair.

It is a further object of the present invention to provide a method of treating hair for improved style retention. These and other objects will become readily apparent from the detailed description which follows.

Unless otherwise indicated, all percentages and ratios herein are by weight.

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SUMMARY OF THE INVENTION

The present invention relates to hair care compositions comprising from about 0.01% to about 10% of a rigid silicone polymer, from about 0.1% to about 99.9% of a volatile carrier or mixtures thereof.

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DETAILED DESCRIPTION OF THE INVENTION

The essential as well as optional components are described below.

Rigid Silicone Polymer

55 The compositions of the present invention contain at least one rigid silicone polymer which when applied to hair imparts style retention benefits.

The polymers comprise from about 0.01% to about 10% of the composition, preferably from about 0.05% to about 7%.

60 Polymers useful in the present invention include, but are not limited to, filler reinforced polydimethyl siloxane gums including those having end groups such as hydroxyl, cross linked siloxanes such as organic substituted silicone elastomers, organic substituted siloxane gums including those having end groups such as hydroxyl, resin reinforced siloxanes and cross linked siloxane polymers.

The rigid silicone polymers useful in the present invention have complex viscosities of at least 2×10^5 poise (P), preferably about 1×10^7 or more, where complex viscosity is measured by subjecting a sample to

oscillatory shear at a fixed frequency of 0.1 rad/sec at 25°C using a Rheometric Fluids Spectrometer® measuring films having a thickness of about 1 millimeter. The resulting viscous and elastic force responses are combined to determine the complex modulus which is divided by the imposed frequency to compute the complex viscosity.

A preferred siloxane gum is a diphenyl-dimethyl polysiloxane gum useful in the invention has a molecular weight of at least about 500,000, and must be diphenyl substituted to the extent of 3% or more, preferably at least about 5%.

The siloxane gums may be filler reinforced to provide additional rigidity. Silica is the preferred filler.

The silicone elastomer useful in the composition of the present invention is that type of material described in U.S. Patent 4,221,688, September 9, 1980 to Johnson et al, incorporated herein by reference. The actual material described in the patent and what is put into the present compositions is an aqueous emulsion which dries to form an elastomer upon removal of the water.

The silicone emulsion has a continuous water phase in which there is a dispersed phase which comprises an anionically stabilized hydroxylated polyorganosiloxane, a colloidal silica and a catalyst. The pH of the emulsion should be in the range of from about 9 to about 11.5, preferably from about 10.5 to about 11.2. The solids content of the emulsion is generally from about 20% to about 60%, preferably from about 30% to about 50%. The amount of colloidal silica present for each 100 parts by weight of the polydiorganosiloxane is from 1 to 150 parts. On the same basis the amount of diorganotindicarboxylate (e.g., dioctyl tindilaureate) catalyst is from 0.1 to 2 parts. The elastomer emulsion is used in an amount of from about 0.1% to about 5%, preferably from about 0.5% to about 4% of the total composition.

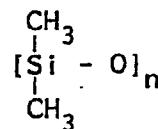
Silicone resins are silicone polymers with a high degree of crosslinking introduced through the use of trifunctional and tetrafunctional silanes. Typical silanes used in the manufacture of resins are monomethyl, dimethyl, monophenyl, diphenyl, methylphenyl, monovinyl, and methylvinyl chlorosilanes, together with tetrachlorosilane. A preferred resin is one offered by General Electric as GE SR545. This resin is provided as a solution in toluene which is stripped prior to the resin's use.

Other rigid silicone polymers of interest are those siloxanes which have been sparingly crosslinked but are still soluble in solvents such as cyclomethicone. Precursors for the rigid material can be any high molecular weight polydimethyl siloxanes, polydimethyl siloxanes containing vinyl groups and other siloxanes. Methods of crosslinking include heat curing with organic peroxides such as dibenzoyl peroxide and di-t-butyl peroxide, heat vulcanization with sulfur and high-energy radiation.

Volatile Carrier

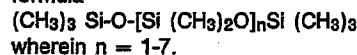
The compositions of the invention comprise a volatile carrier, or mixtures thereof, which preferably is present from about 0.1% to about 99.9% for the silicone polymer. The term "volatile" as used herein means that the material has a measurable vapor pressure.

Where the rigid silicone polymer is a polydimethyl siloxane or a polydiphenyldimethyl siloxane, the preferred carriers are volatile silicones having a boiling point between 99°C to about 260°C and have a solubility in water of less than about 0.1%. The degree of substitution on the siloxane (higher substitution, lower solubility) obviously affects the polymer's solubility and is taken into account by the formulator. The silicones may be either cyclic or linear polydimethyl siloxanes. The number of silicone atoms in the cyclic silicones is about 3 to about 7, most preferably 4 or 5. The general formula for cyclic silicones is:



wherein n = 3-7. Viscosities are generally less than 10 centipoise (cP) at 25°C.

Linear polydimethyl siloxanes useful in the invention generally have viscosities of about less than about 5cP at 25°C. The linear volatile silicones contain from about 3 to about 9 silicone atoms and have the general formula



Silicones of the above described types are widely available e.g., from Dow Corning as 344,345 and 200 fluids; Union Carbide as Silicone 7202 and 7158, and Stauffer Chemical as SWS-03314.

Also useful in compositions of the invention are certain volatile hydrocarbons. These hydrocarbons may be either straight chain or branched, and contain from about 10 to about 16 carbon atoms, preferably from about 12 to about 16 carbon atoms.

Water is also useful in compositions of the present invention either alone or in mixtures with other volatile carriers. Where the elastomer alone is used, water may be preferred and if so, a surfactant, as described below, is also present.

Short chain alcohols such as ethanol are also suitable solvents for use in the present compositions.

Optional IngredientsSurfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from about .05% to about 50%. For a shampoo, the level is preferably from about 10% to about 30%, most preferably from about 12% to about 25% of the composition. For conditioners the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

Synthetic anionic detergents useful herein, particularly for the shampoo compositions, include alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ wherein R is alkyl or alkenyl or about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having about 10 to about 20 carbon atoms. Preferably, R has 12 to 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with 1 to 10, and especially 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates of the present invention are sodium coconut alkyl triethylene glycol ether sulfate; lithium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to 16 carbon atoms and an average degree of ethoxylation of from about 1 to 4 moles of ethylene oxide. Such a mixture also comprises from about 0 to 20% by weight C₁₂₋₁₃ compounds; from 60 to 100% by weight of C₁₄₋₁₅₋₁₆ compounds, from about 0 to 20% by weight of C₁₇₋₁₈₋₁₉ compounds; from about 3 to 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to 90% by weight of compounds having a degree of ethoxylation of from 1 to 4; from about 10 to 25% by weight of compounds having a degree of ethoxylation of from 4 to 8; and from about 0.1 to 15% by weight of compounds having a degree of ethoxylation greater than 8.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:

$\text{R}_1-\text{SO}_3\text{-M}$

wherein R₁ is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from 8 to 24, preferably 12 to 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having 8 to 24 carbon atoms, preferably 12 to 18 carbon atoms and a sulfonating agent e.g., SO₃, H₂SO₄, oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C₁₂₋₁₈ n-paraffins.

Additional examples of anionic synthetic detergents which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, or example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfo-succinamate; diethyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic detergents utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO₂, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO₂, etc., when used in the gaseous form.

The α -olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

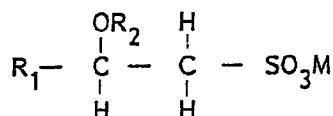
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A specific α -olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,322,880 of Phillip F. Pflaumer and Adrian Kessler, Issued July 25, 1967, titled "Detergent Composition", the disclosure of which is incorporated herein by reference. 5

Another class of anionic organic detergents are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from 6 to 20 carbon atoms, R_2 is a lower alkyl group having from 1 (preferred) to 3 carbon atoms, and M is a water-soluble cation as hereinbefore described. 10

Specific examples of β -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein to provide superior cleaning levels under household washing conditions include: potassium β -methoxydecanesulfonate, sodium 2-methoxytridecanesulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecylsulfonate, sodium β -methoxyoctadecylsulfonate, and ammonium β -n-propoxypentadecylsulfonate. 15

Many additional nonsoap synthetic anionic surfactants are described in McCUTCHEON'S, DETERGENTS AND EMULSIFIERS, 1984 ANNUAL, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, to Laughlin et al., issued December 30, 1975 discloses many other anionic as well as other surfactant types and is incorporated herein by reference. 20

Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are: 25

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example. 30

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory. 35

3. The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms. 40

4. Long chain tertiary amine oxides corresponding to the following general formula: 45



wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to 1 glyceryl moiety, and R_2 and R_3 contain from 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxy ethyl, or hydroxy propyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethylidodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decyldamine oxide, dimethyltetradecylamine oxide, 3,6,9-trioxaheptadecyl diethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dode-coxyethylidimethylamine oxide, 3-dodecoxy-2-hydroxypropylid(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide. 55

5. Long chain tertiary phosphine oxides corresponding to the following general formula: 60



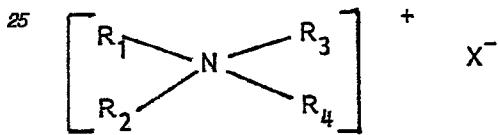
wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from 8 to 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecidimethylphosphine oxide, tetradecylidimethylphosphine oxide, tetradecylmethyllethylphosphine oxide, 3,6,9-trioxaoctadecylidimethylphosphine oxide, cetylidimethylphosphine oxide, 3-dodecoxy-2-hy- 65

droxypropyl(2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cetylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyltriethylphosphine oxide, tetradecyltriethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldihydroxymethylphosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which contain alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

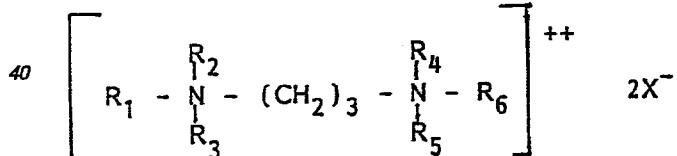
Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactant vehicle materials among those useful herein are disclosed in the following documents, all incorporated by reference herein: M. C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich Jr., Issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R₁ is hydrogen, an aliphatic group of from 1 to 22 carbon atoms, or an aromatic, aryl or alkylaryl group having from 12 to 22 carbon atoms; R₂ is an aliphatic group having from 1 to 22 carbon atoms; R₃ and R₄ are each alkyl groups having from 1 to 3 carbon atoms, and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amido groups.

Other quaternary ammonium salts useful herein are of the formula



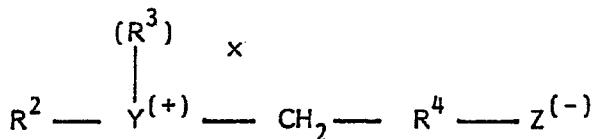
wherein R₁ is an aliphatic group having from 16 to 22 carbon atoms, R₂, R₃, R₄, R₅ and R₆ are selected from hydrogen and alkyl having from 1 to 4 carbon atoms, and X is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein in the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid. (Tallow fatty acids give rise to quaternary compounds wherein R₁ and R₂ have predominately from 16 to 18 carbon atoms.) Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant vehicle materials. The alkyl groups of such amines preferably have from 12 to 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl

stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidyl behenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate and N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants include among these useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981 (incorporated by reference herein.)

Zwitterionic surfactants, useful in shampoos as well as conditioners, can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R² contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R³ is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom; R⁴ is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples include:

- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradexocylphosphonio]-2-hydroxypropane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxypentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxy-ethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxy-ethyl) carboxy methyl betaine, stearyl bis-(2-hydroxy-propyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl) alpha-carboxyethyl betaine, etc. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxy-ethyl) sulfopropyl betaine and the like; amido betaines and amidosulfobetaines, wherein the $\text{RCONH(CH}_2\text{)}_n\text{}$ radical is attached to the nitrogen atom of the betaine are also useful in this invention. The amido betaines are preferred for use in some of the compositions of this invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

The above-mentioned surfactants can be used alone or in combination in the hair care compositions of the present invention. The alkyl sulfates, the ethoxylated alkyl sulfates and mixtures thereof are preferred for use herein.

Where the hair care compositions are conditioner compositions, preferred optional components include gel vehicle materials. The vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Such gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodily Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodily Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems

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Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

Lipid vehicle material:

5 The vehicles incorporate one or more lipid materials, (herein referred to as comprising a "lipid vehicle material", singly or in combination) which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from 12 to 22, preferably from 16 to 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

10 Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3d edition, D. Swern, ed. 1979) (incorporated by reference herein). Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarín, et al., issued May 26, 1981; British Specification 1,532,585, published

15 November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-102 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1967 (incorporated by reference herein.)

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

20 Other vehicles, suitable for use with the rigid silicones herein are, for example, tonics, mousse and hairsprays. Tonics utilize a solvent such as water or alcohol while mousse and hairsprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, dimethyl ether, propane, n-butane or isobutane in addition to the rigid silicone and optional components as set forth below. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% for mousse and from about 15% to about 40% for hairsprays.

25 The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more acceptable. Such conventional optional ingredients are well known to those skilled in the art, e.g., pearlescent aids such as ethylene glycol distearate; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers such as a diethanolamide of a long chain fatty acid (e.g. PEG 3 lauric diethanolamide), cocmonoethanol amide, dimethicone copolyols, guar gum, methyl cellulose starches and starch derivatives, fatty alcohols such as cetearyl alcohol, sodium chloride, sodium sulfate, polyvinyl alcohol, and ethyl alcohol; pH adjusting agents such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate, etc.; coloring agents such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents such as hydrogen peroxide, perborate and persulfate salts, hair reducing agents such as the thioglycolates; perfumes; and, sequestering agents such as disodium ethylenediamine tetraacetate, polymer plasticizing agents such as glycerin and propylene glycol. Such agents generally are used individually at a level of from about 0.01% to about 10%, preferably from about 0.05% to about 5.0% by weight of the composition.

30 40 The pH of the present compositions is not critical and may be in the range of from about 3 to about 10. As with all compositions, the present compositions should not contain components which unduly interfere with the performance of the compositions.

METHOD OF MANUFACTURE

45 Methods of manufacture of various types of hair care compositions are described in the following examples.

INDUSTRIAL APPLICABILITY

The present compositions are used in a conventional manner varying with the type of composition described.

50 The following Examples further illustrate the preferred embodiments within the scope of the present invention. The Examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

55 **EXAMPLE 1**

Shampoo Compositions

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<u>Component</u>	<u>Weight %</u>	
Ammonium lauryl sulfate	8.59	5
EDTA	0.20	
Citric acid	0.79	10
Sodium hydroxide	0.75	
Cocamide MEA	1.00	
Glycol distearate	1.50	15
Ammonium laureth-3 sulfate	12.09	
Cetearyl alcohol	0.10	
Silicone premix (see examples) ¹		20
Preservative	0.03	
Fragrance	0.30	
Distilled water	q.s.	25

¹: Level of silicone premix varies with selection

Silicone Premixes:	I	II	III	IV	
D-5 cyclomethicone	1.50	--	1.50	1.50	30
Polydimethyl siloxane ¹	1.50	--	0.30	--	
Silica ²	0.26	--	--	--	
Silicone elastomer ³	--	3.00	--	--	35
Purified resin ⁴	--	--	0.60	--	
Diphenyldimethyl siloxane gum ⁵	--	--	--	1.50	40

¹: SE-76 gum, supplied by General Electric Company

²: Cab-O-Sil HS-5, supplied by Cabot Corporation

³: Silicone elastomer Q3-5205, supplied by Dow Corning Corporation

⁴: SR-545 resin, supplied by General Electric Company

⁵: SE54 gum supplied by General Electric Company

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5 I: The polydimethyl siloxane and silica are intimately mixed in a high shear ribbon mix for at least 2 hours. The blend is then dissolved in the D-5 cyclomethicone to form the silicone premix.

10 II. The silicone elastomer is added directly to the batch.

15 III. The resin is received as a solution in toluene. The toluene is stripped completely, and the purified resin is dissolved with the polydimethylsiloxane in the cyclomethicone.

20 15 Ammonium lauryl sulfate, EDTA, citric acid, and sodium hydroxide are added to the distilled water at about 15°C. The mixture is heated to from 70°C to 80°C. The cocamide MEA and glycol distearate are added at this point. The ammonium laureth-3 sulfate, cetearyl alcohol and silicone premix are blended at from 70°C to 90°C. This mixture is added to the batch following the glycol distearate. The preservative is then added. The batch is mixed for 5 minutes then cooled to room temperature (15°C to 25°C). The fragrance is added, then the batch is milled under high shear for at least 5 minutes using conventional milling apparatus.

EXAMPLE 2

25 Mousse Compositions

The following composition was prepared:

	<u>Component</u>	<u>Weight %</u>
30	Luviskol® VA55E (50% active) ¹	9.00
	Propylene glycol	2.00
35	Carbopol® 934 ²	0.20
	Cocodimethyl amine oxide	0.25
	Aminomethyl propanol	0.30
40	Glydant® ³	0.37
	Perfume	0.10
45	D.C.Q3-5025 silicone elastomer (40% active) ⁴	2.50
	A-46 propellant ⁵	10.00
	Double reverse osmosis water	q.s. 100%

1 PVP/PVA Copolymer offered by BASF

2 Carboxyvinyl polymer offered by B.F. Goodrich Co.

3 Preservative offered by Glyco Chemical Co.

4 Silicone elastomer offered by Dow Corning

5 A mixture of propane (20%), Isobutane (78%) and n-butane (2%) offered by Phillips Petroleum Company

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EMI PA=21 FR=1 HE=40 WI=125 TI=TAB

65 The aerosol mousses of the present invention are prepared by combining all ingredients except the aerosol propellant into a batch called the concentrate. This concentrate is made by slurring the Carbopol with agitation in the water for several minutes until there are no Carbopol lumps. To this is added the aminomethyl

propanol while increasing the agitator speed to accommodate the increase in viscosity accompanying neutralization. Maintaining vigorous agitation, the remaining ingredients except for Glydant and silicone elastomer are added and mixed until well dispersed. The Glydant and silicone elastomer are finally added and mixing continued until these are thoroughly dispersed. The resulting concentrate is very thick with a pH of 8.2. Aerosol mousse cans are prepared by placing 135 grams of concentrate into 5 oz. aluminum monobloc (epoxy lining) cans, placing mousse valves on can tops, drawing a vacuum to evacuate can headspace (to remove air), and crimping the valve into place. The propellant (15 grams) is added by pressure filling through the valve stem.

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EXAMPLE 3

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This is another example of a composition which was prepared.

<u>Component</u>	<u>Weight %</u>	
Luviskol K-30 ¹ (30% active)	2.00	15
Xanthan gum	0.70	
Glydant	0.37	
Nonoxynol-14	1.00	20
D.C. Q3-5024 silicone elastomer (40% active) ²	1.00	
A-70 propellant ³	5.00	25
Double reverse osmosis water	q.s. 100%	
¹ PVP polymer offered by BASF		
² Silicone elastomer offered by Dow Corning		30
³ A mixture of propane and isobutane offered by Phillips Petroleum Company		
		35

EXAMPLE 4

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The following is another mousse composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>	
Cantrez® ES 225 ¹ (50% active)	4.00	
Carbopol 941	0.20	45
Aminomethyl propanol	0.80	
Glydant	0.37	
A-46	8.00	50
D.C. Q3-5024 silicone elastomer (40% active)	.50	
Double reverse osmosis H ₂ O	q.s. 100%	55

¹ Copolymer of methylvinyl ether/maleic anhydride offered by GAF

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EXAMPLE 5Conditioner Compositions

A hair conditioner, according to the present invention, was made comprising:

	<u>Component</u>	<u>Weight %</u>
5	Hydroxyethyl cellulose	0.50
10	Quaternium-18 ¹	0.85
15	Dimethicone copolyol ²	0.10
20	Cetyl alcohol	1.00
25	Stearyl alcohol	0.75
30	Ceteareth-20	0.35
35	Stearamidopropyl dimethylamine ³	0.50
40	Glycerol monostearate	0.25
45	Citric acid	0.13
50	Fragrance	0.20
55	Preservative	0.03
60	Rigid silicone premix ⁴ (see examples)	--
65	Distilled water	q.s. 100%

1: Adogen 442-100P, Sherex Chemical Company
 2: Dow Corning 190 Silicone Surfactant
 3: Lexamine S-13, Inolex Corporation
 4: Amount varies with type of premix selected

Rigid Silicone Premix Examples

	<u>Component</u>	<u>Weight %</u> (total batch)
45	Polydimethylsiloxane ¹	0.30
50	Silica ²	0.05
55	D-5 cyclomethicone	1.70

1: SE-76 gum, General Electric Company
 2: Cab-O-Sil HS-5, Cabot Corporation

The polydimethyl siloxane and silica are intimately mixed for at least 4 hours in a high shear ribbon mixer. The resulting blend is dissolved in the cylcomethicone to form the premix used in the base formula.

<u>Component</u>	<u>Weight %</u> (total batch)
Polydiphenyldimethyl siloxane ¹	0.30
D-5 cyclomethicone	1.70
¹ : SE-54 gum, General Electric Company	

The polydiphenyl dimethyl siloxane is dissolved in the cyclomethicone to form the premix used in the base formula.

In place of the gum, a silicone resin may be used to form another premix.

Hydroxyethyl cellulose is added to the distilled water at a temperature of 15°C to 40°C. This mixture is well dispersed, then heated to a temperature of from 60°C to 90°C. Materials 2 through 8 are added to the batch while the temperature is maintained in this range. The mixture is stirred for approximately 10 minutes, then cooled to approximately 50°C. The remaining materials are added to this temperature. The mixture is milled under high shear for approximately 2 minutes using a conventional milling apparatus, then cooled to room temperature and collected.

EXAMPLE 6

A conditioner composition according to the present invention, is as follows:

<u>Component</u>	<u>Weight %</u>
Hydroxyethyl cellulose	0.50
Quaternium-18	0.40
Dimethicone copolyol	0.10
Cetyl alcohol	1.00
Stearyl alcohol	0.75
Ceteareth-20	0.35
Stearamidopropyl dimethylamine	0.50
Glyceryl monostearate	0.25
Citric acid	0.13
Fragrance	0.20
Preservative	0.03
Silicone elastomer ¹	1.00
Double reverse osmosis water	q.s. 100%

¹: Silicone Elastomer Q3-5205, Dow Corning Corporation

A hair conditioning product, as comprised above, was made in a manner similar to that described in the base formula. This product, when applied to human hair, is useful as a hair conditioner. The silicone elastomer is added directly to the base formula.

EXAMPLE 7

An aerosol hairspray composition of the present invention is as follows:

	<u>Component</u>	<u>Weight %</u>
5	A-31 Propellant ¹	75.00
	SDA40 200 proof ethanol	22.00
	Silicone premix	3.00

	<u>Silicone Premix</u>	<u>Parts</u>
10	Polydimethyl siloxane ²	2.50
	Silica ³	.50

15 ¹: Isobutane offered by Phillips Petroleum Company
 2: SE-76 gum, supplied by General Electric Company
 3: Cab-O-Sil HS-5, Cabot Corporation

20 The polydimethyl siloxane and silica are intimately mixed in a high shear ribbon mixer for at least 4 hours.
 Aerosol hairspray cans are then prepared by adding 3 grams of silicone premix and 22 grams SDA40 200 proof ethanol to the aerosol can, placing valves on can tops, drawing a vacuum to evacuate can headspace (to remove air), and crimping valves into place. The propellant (75 grams) is added by pressure filling through the valve stem.

A premix containing 1% of the siloxane gum and 2% of purified resin SR545 may be used in place of the above-described premix.

30 EXAMPLE 8
 The following is a pump spray tonic composition of the present invention:

	<u>Component</u>	<u>Weight %</u>
35	DIC Q3-5025 silicone	4.00
	Elastomer (40% active)	
	Sodium lauryl sulfate	0.20
40	Glydant	0.37
	Perfume	0.01
	Double reverse osmosis water	q.s. to 100%

45 The ingredients are added in order, water, sodium lauryl sulfate, perfume, Glydant, and silicone elastomer. The batch is mixed at ambient temperature for 20 minutes. The batch is then placed in pump bottle.

50 EXAMPLE 9
 The following is a styling composition of the present invention:

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<u>Component</u>	<u>Weight %</u>	
SDA 40 ethanol	40.00	
Cyclomethicone (D ₅)	2.00	5
Silicone gum ¹	.05	
Benzoyl peroxide	.00005	
Fragrance	.05	10
Double reverse osmosis water	q.s. 100%	

The silicone premix is prepared by first crosslinking the silicone gum with benzoyl peroxide. This is accomplished by thoroughly blending the benzoyl peroxide into the silicone gum with a ribbon or other suitable mixer. This mixture is then heated to about 150°C for twenty minutes. The result crosslinked gum is then mixed with the cyclomethicone for several hours until it has fully dispersed. 15

The tonic itself is prepared by simply adding the premix to the water, fragrance, and ethanol.

1: SE76 offered by General Electric

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EXAMPLE 10

The following is another hair tonic composition of the present invention:

<u>Component</u>	<u>Weight %</u>	
Ethanol (SDA 40)	40.0	25
D-4 cyclomethicone [±]	1.56	
Dimethicone gum ¹	0.013	30
Silica ²	0.0024	
Fragrance	0.20	
Water	q.s. 100%	35
¹ : SE-76 from General Electric		
² : Cab-O-Sil HS-5 from Cabot		40

The silica and dimethicone gum are intimately mixed for at least 2 hours in a high shear ribbon mixer. This compound is then dissolved in the cyclomethicone. This blend is added to the rest of the tonic formula. 45

EXAMPLE 11

The following is another hair tonic composition of the present invention:

<u>Component</u>	<u>Weight %</u>	
Ethanol (SDA 40)	40.0	50
D-5 cyclomethicone	2.0	
Polydiphenyldimethyl siloxane ¹	0.05	55
Fragrance	0.20	
Water	q.s. 100%	
¹ : SE-54, General Electric		60

The polydiphenyl dimethyl siloxane is dissolved in the cyclomethicone. This blend is added to the rest of the tonic formula. 65

EXAMPLE 12

The following is yet another hair tonic composition of the present invention:

	<u>Component</u>	<u>Weight %</u>
5	Fragrance [±]	0.2
10	Ethanol (SDA 40)	30.0
15	D-5 cyclomethicone	1.5
20	Dimethicone gum ¹	0.187
25	Purified resin SR545 ²	0.375
30	Water	q.s.100%

1: SE-76, General Electric
 2: The resin is received as a solution in toluene from General Electric. The toluene is stripped completely, and the purified resin is dissolved at 50% in cyclomethicone. The dimethicone is also dissolved in a separate solution with cyclomethicone. The two solutions are blended together. This mixture is added to the rest of the formula.

Claims

- 35 1. A hair care composition comprising:
 a) from about 0.01% to about 10% of a rigid silicone polymer having a complex viscosity of at least 2×10^5 poise; and
 b) a volatile carrier
 wherein if water is the sole carrier a surfactant is also present.
- 40 2. A hair care composition according to Claim 1 wherein the rigid silicone polymer is selected from the group consisting of organic substituted siloxane gums, silicone elastomers, filler reinforced dimethyl siloxane gums, resin reinforced siloxanes and crosslinked siloxane polymers.
- 45 3. A hair care composition according to Claims 1 or 2 wherein the volatile carrier is a cyclic silicone containing from about 3 to about 7 silicon atoms.
- 4. A hair care composition according to Claim 1 or 2 wherein the volatile carrier is water.
- 5. A hair care composition according to Claims 1, 2 or 4 in the form of a shampoo which additionally contains a synthetic surfactant.
- 6. A hair care composition according to Claim 5 wherein the rigid silicone polymer is a silica reinforced dimethyl siloxane gum.
- 7. A hair care composition according to Claims 1, 2, 3 or 4 in the form of a conditioner.
- 8. A hair care composition according to Claim 7 which in addition contains a lipid material and a cationic surfactant.
- 9. A hair care composition according to Claims 1, 2, 3 or 4 in the form of a hair tonic.
- 10. A hair care composition according to Claims 1, 2, 3 or 4 in the form of a hairspray.
- 55 11. A hair care composition according to Claims 1, 2, 3 or 4 in the form of a mousse.
- 12. A hair care composition comprising:
 a) from about 0.05% to about 7% of a rigid silicone polymer selected from the group consisting of filler reinforced polydimethylsiloxane polymers, silicone elastomers and polydiphenyl-dimethyl siloxane polymers; and
 b) a volatile carrier.



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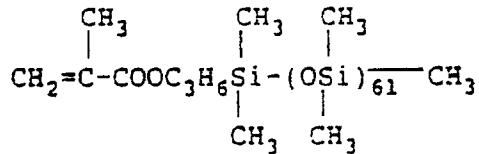
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(54) Polymer for hair-care products.

(57) A polymer suitable for use in hair care products comprising a copolymer comprising
(a) a unit of a hydrophilic ethylenically unsaturated monomer such as dimethylaminoethyl methacrylate in a quantity of 15 to 99.9% by weight;
(b) a unit of an ethylenically unsaturated monomer having a polysiloxane group such as:



in a quantity of 0.1 to 85% by weight; and (c) a unit of an optional hydrophobic unsaturated monomer such as lauryl methacrylate in a quantity of 0 to 84.9% by weight.

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POLYMER FOR HAIR-CARE PRODUCTS

The present invention relates to novel polymers suitable for use in hair-care products. More particularly, the present invention relates to a polymer comprising as an essential constituent units of a hydrophilic unsaturated monomer which affords hair an excellent brilliance and gloss and a smooth feeling and has an excellent washability, and into which a polysiloxane group has been introduced.

5 The polymers in accordance with the present invention can be used for providing hair with settability, softness, gloss, smooth feeling, smooth combing, recovery from damages, manageability and the like.

In hair-care products such as a shampoo, a rinse, a hair treatment product, a hair setting product or a cold permanent wave solution have heretofore been used oily components such as silicone compounds, ester compounds, hydrocarbon compounds or the like in an emulsified, solubilized or dissolved state, for

10 the purpose of providing hair with brilliance, gloss and smoothness. The silicone type compounds among them have these years been used extensively because of their excellent properties.

Specifical examples of application of silicone compounds include (i) hair-care products into which silicone oils such as polydimethylsiloxane, polymethylphenylsiloxane or the like and their emulsion have been incorporated; (ii) aerosol foam type hair setting products such that an etherified silicone such as a

15 polydimethylsiloxane-polyoxyalkylene block copolymer or the like has been incorporated into a hair-fixative polymer such as a cationic polymer or an amphoteric polymer to form, together with a propellant, the aerosol products (Japanese Patent Laid-Open Publication No. 135319/88); (iii) shampoos and rinses into which an aminated organopolysiloxane emulsion has been incorporated (Japanese Patent Laid-Open Publication No. 307811/63); (iv) hair conditioning product and hair-setting products such that an aminated

20 organopolysiloxane emulsion has been incorporated into a cationic polymer compound and an amphoteric polymer compound, respectively, to form the hair conditioning product and hair-setting products (Japanese Patent Laid-Open Publication No. 275515/88); and (v) hair-care products in which polydimethylsiloxane or polymethylphenylsiloxane having a high molecular weight is used (Japanese Patent Laid-Open Publication No. 243019/88).

25 However, the silicone oils or the etherified silicones when used may cause problems such as giving sticky feeling to hair or undergoing reverse transition of silicone from hair to hand or clothing if they are formulated in a large amount or if the product is used repeatedly for a long time. Emulsions of silicones may have problems in dispersion stability. Silicones having a high molecular weight may have problems in the compatibility with hair care resins or additives, so that they have restrictions in formulation whereby their

30 applicability in a variety of hair-care products is restricted.

The silicone compounds having no such hydrophilic groups as a polyether group are difficult to be removed by usual hair washing, and thus when consumers use the products into which the less hydrophilic silicone compounds have been formulated for a long period repeatedly, hair tends to be hydrophobic and causes problems in hair dyeing or permanent waving.

35 The object of the present invention is to solve the aforementioned problems and to provide a novel polymer for hair-care products which provides hair with an excellent gloss and brilliance and a smooth feeling without stickiness and will not be accumulated in the hair and cause no problems for being formulated into cosmetics.

The polymer suitable for use in hair-care products according to the present invention comprises a
40 copolymer comprising (a) a unit of a hydrophilic ethylenically unsaturated monomer in a quantity of 15 to 99.9% by weight; (b) a unit of an ethylenically unsaturated monomer having a polysiloxane group in a quantity of 0.1 to 85% by weight; and (c) a unit of a hydrophobic ethylenically unsaturated monomer in a quantity of 0 to 84.9% by weight.

In the present invention, an ethylenically unsaturated monomer having a polysiloxane group (b) is
45 copolymerized with a hydrophilic ethylenically unsaturated monomer (a) and, if necessary, with a hydrophobic ethylenically unsaturated monomer (c), so that the defects in conventional silicone compounds such as generation of the sticky feeling of hair or the reverse transition of silicone encountered when the silicone compounds are formulated in a large quantity or on the use for a long period repeatedly can be solved thanks primarily to the use of the compound (b), and the silicone can be easily removed by washing hair
50 thanks primarily to the component (a). Further, a hydrophilic ethylenically unsaturated monomer component (a) and a hydrophobic ethylenically unsaturated monomer component (c) are appropriately chosen in terms of their types and relative proportions, so that the polymer can now be incorporated into hair care products without restriction.

DESCRIPTION OF THE PREFERRED EMBODIMENT OF THE INVENTION

5

[I] Polymer

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Unsaturated Monomer

The polymer suitable for use in the present invention is obtained by copolymerizing two essential monomers, namely (a) a hydrophilic unsaturated monomer and (b) an unsaturated monomer having a polysiloxane group, and an optional monomer, namely (c) hydrophobic unsaturated monomer. Each of these monomers of the categories (a), (b) and (c) can be used in admixture within respective categories.

Hydrophilic unsaturated monomers (a):

20 Preferably, the hydrophilic unsaturated monomers as the component (a) are hydrophilic unsaturated monomers of a cationic, anionic, nonionic or amphoteric nature and polymerizable through radical polymerization mechanism. It is preferable that they have a solubility in water in a range of 10 g/100 g of water or more (25 °C).

Examples of the cationic unsaturated monomers include

25 (i) monomers derived from acrylic acid or methacrylic acid, which is referred to hereinafter collectively as (meth)acrylic acid, and a quaternarized epihalohydrin product of a trialkylamine having 1 to 4 carbon atoms in the alkyl such as (meth)acryloyloxyhydroxypropyltrimethylammonium chloride and (meth)-acryloyloxyhydroxypropyltriethylammonium bromide;

30 (II) amine derivatives of (meth)acrylic acid or amine derivatives of (meth)acrylamide derived from (meth)-acrylic acid or (meth)acrylamide and a dialkylalkanolamine having C₁ to C₄ alkyl groups such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)-acrylate, or dimethylaminopropyl (meth)acrylamide; and

35 (iii) derivatives of the products of the group (ii) above by (1) neutralization with an acid such as hydrochloric acid, or lactic acid, (2) denaturation with a halogenated alkyl such as methyl chloride, ethyl chloride, methyl bromide, or ethyl iodide, (3) denaturation with a halogenated fatty acid ester such as ethyl monochloroacetate, or methyl monochloropropionate, and (4) denaturation with a dialkyl sulfate such as dimethyl sulfate, or diethyl sulfate.

Furthermore, the cationic unsaturated monomers include amine derivatives of allyl compounds such as dialyldimethylammonium chloride and the like.

40 These cationic unsaturated monomers can be copolymerized in the form as such, or as an alternative they can be copolymerized in the form of their precursors, which are then cationized by a so-called cationizing agent. More particularly, dimethylaminoethyl (meth)acrylate is copolymerized, and the copolymer obtained will then be cationized by a quaternizing agent such as hydrochloric acid, ethyl monochloroacetate, dimethyl sulfate or the like to form a desired copolymer of the cationic unsaturated monomer.

45 Examples of the anionic unsaturated monomers include:

(i) unsaturated carboxylic acid monomers such as (meth)acrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid, and crotonic acid;

50 (ii) half esters of an unsaturated polybasic acid anhydride such as succinic anhydride, phthalic anhydride or the like with a hydroxyl group-containing (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate or the like,

(iii) monomers having a sulfonic acid group such as styrenesulfonic acid, sulfoethyl (meth)acrylate or the like, and

(iv) monomers having a phosphoric acid group such as acid phosphooxyethyl (meth)acrylate, 3-chloro-2-acid phosphooxypropyl (meth)acrylate or the like.

These anionic unsaturated monomers can be used in the form of an acid or after partial or complete neutralization, or they can be copolymerized in the form of acid and then neutralized partially or completely. Examples of the bases used for neutralization include alkali metal hydroxides such as lithium hydroxide,

potassium hydroxide, sodium hydroxide or the like, aqueous ammonia, amine compounds such as mono-, di- or triethanolamine, triethylamine, morpholine, aminomethylpropanol, aminoethylpropanediol or the like.

Examples of the nonionic unsaturated monomers include monomers derived from (meth)acrylic acid or (meth)acrylamide and an alkylene oxide having 2 to 4 carbon atoms such as hydroxyethyl (meth)acrylate, polyethyleneglycol mono(meth)acrylate, methoxypolyethyleneglycol mono(meth)acrylate, methoxypoly(ethylene glycol/propylene glycol) mono(meth)acrylate, polyethylene glycol di(meth)acrylate, N-polyalkylenoxy(meth)acrylamide or the like; acrylamide, N-vinylpyrrolidone or the like.

Examples of the amphoteric monomers include zwitter ionized derivatives of the aforementioned amine derivatives of (meth)acrylic acids or the amine derivatives of (meth)acrylamide such as dimethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acrylamide by a halogenated fatty acid salt such as potassium monochloroacetate, sodium monobromopropionate, aminomethylpropanol salt of monochloroacetic acid, triethanolamine salt of monochloroacetic acid and the like; and modified products with propanesultone of the aforementioned amine derivatives of (meth)acrylic acid or (meth)acrylamide.

These amphoteric unsaturated monomers, like the aforementioned cationic unsaturated monomers, can be copolymerized in the form as such or as an alternative they can also be copolymerized in the form of their precursors, which are then converted into amphoteric state. It is also possible to remove the salt produced as a by-product of amphoteration by filtration or ion-exchange, if necessary, before copolymerization step or after the copolymerization-amphoteration step. These technologies is described in detail in Japanese Patent Laid-Open Publication No. 92809/81.

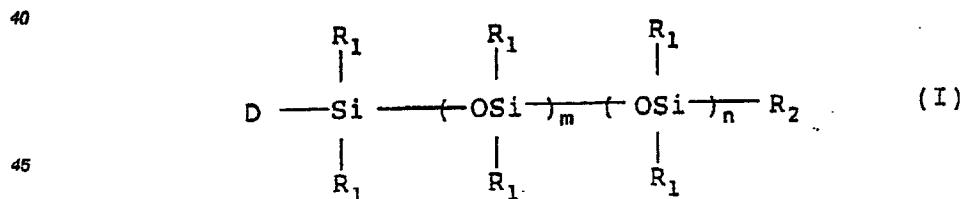
The hydrophilic unsaturated monomer is used in an amount of 15 to 99.9% by weight per weight of total monomers. If the amount is less than 15% by weight, the copolymer thus obtained has problems that it is hardly soluble in water and/or an ethanolic solvent or it is difficult to be removed upon hair washing. The amount of the monomer can be selected at will according to the uses with the upper limit of 99.9% by weight. In other words, the hydrophilic unsaturated monomer is preferably used in an amount of 15 to 59.5% by weight when the polymer is used as a hair-setting polymer and 30 to 99.5% by weight when the polymer is used as a hair-conditioning polymer. Polysiloxane group containing unsaturated monomer (b):

The polysiloxane group-containing unsaturated monomer as the component (b) is a monomer which has at least one unsaturated group having radical polymerizability and a polysiloxane group



wherein $a = 1$ to 150.

Specifically, compound represented by the following formula (I) are mentioned:



wherein D, R₁, R₂, m and n have the following meanings, respectively:

50 D = an unsaturated group having radical polymerizability such as a vinyl group, a vinylalkylene group, a vinylhydroxyalkylene group, an acryloyloxyalkylene group or a methacryloyloxyalkylene group;

R₁ = a hydrogen atom, a phenyl group, an alkyl group having 1 to 10 carbon atoms, a polyoxyalkylene group, a polyoxyalkylene group of which end has been substituted by an ether or ester group, a polyalkylenepolyamine group, a fatty acid group or a polysiloxane group, respectively;

55 R₂ = a hydrogen atom, a phenyl group, an alkyl group having 1 to 10 carbon atoms, a polyoxyalkylene group, a polyoxyalkylene group of which end has been substituted by an ether or ester group, a polyalkylenepolyamine group, a fatty acid group or a polysiloxane group, or an unsaturated group having radical polymerizability such as a vinyl group, a vinylalkylene group, a vinylhydroxyalkylene group, an

acryloyloxyalkylene group or a methacryloyloxyalkylene group;

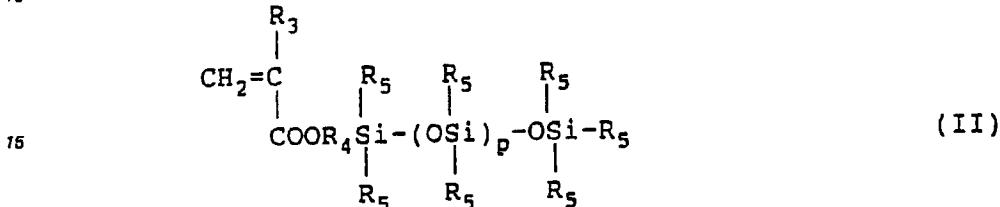
m = an integer from 4 to 150; and

n = an integer from 0 to 150, wherein the sum of m and n is within 150.

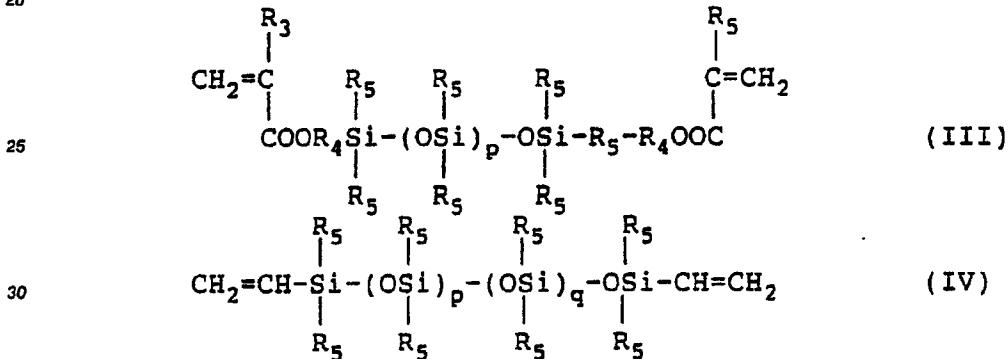
In the above-described formula (I), the sum of m and n is preferably in the range of 4 to 150. If the sum is less than 4, the polymer obtained by the copolymerization cannot exhibit the advantages inherent in the silicone compound. If the sum exceeds 150, the copolymerizability with the unsaturated monomers of the components (a) and (b) is undesirably lowered.

Embodiments of the unsaturated monomer having a polysiloxane group include the unsaturated monomers illustrated by the following formulae (II) - (IV):

10



20



35 wherein R_3 - R_5 , p and q have the following meanings independently of each other between the formulae:

R_3 = a hydrogen atom or a methyl group;

R_4 = an alkylene group having 1 to 4 carbon atoms;

R_5 = an alkyl group having 1 to 10 carbon atoms or a phenyl group;

p = an integer of 1 or more; and

40 q = an integer of 1 or more, wherein the sum of p and q are within 150.

The unsaturated monomers illustrated by the general formula (II) can be obtained as commercially available products (manufactured by Chisso Corporation) such as FM0711 (trade name; p = 10, R_3 = a methyl group, R_4 = a propylene group, and R_5 = a methyl group in the aforementioned formula (II); referred to as polysiloxane FM0711 in the preparation example below), FM0721 (p = 60, R_3 = a methyl group, R_4 = a propylene group, and R_5 = a methyl group in the aforementioned formula (II); referred to as polysiloxane FM0721 in the preparation example below) and FM0725 (p = 130, R_3 = a methyl group, R_4 = a propylene group, and R_5 = a methyl group in the aforementioned formula (II); referred to as polysiloxane FM0725 in the preparation example below).

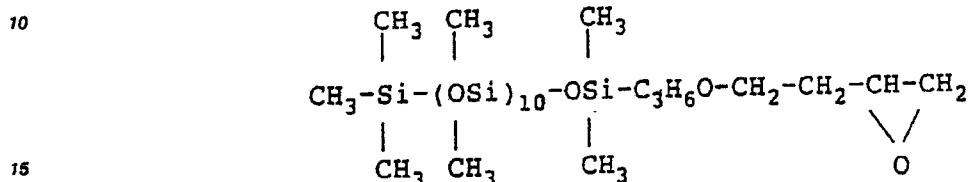
The monomers illustrated by the general formula (III) can be easily obtained by the reaction of a 50 polysiloxane having both ends of silanol and a (meth)acryloyloxyalkylene (having 1 to 4 carbon atoms) di(alkyl (having 1 to 4 carbon atoms) or phenyl) halosilane.

The unsaturated monomers illustrated by the general formula (IV) can be obtained as commercially available products (manufactured by Chisso Corporation) such as FP2231 (trade name; p = 30, q = 5, R_5 = a methyl group and R_6 = a phenyl group; referred to as polysiloxane FP2231 in the preparation example below), FP2241 and FP2242.

The polysiloxane group-containing unsaturated monomers illustrated by the general formulae (II) - (IV) can be copolymerized in the form as such. Alternatively, they can copolymerized in the form of their precursor and a polysiloxane group will then be added. Specifically, a polysiloxane group can be introduced

by copolymerizing the monomer in the form of (meth)acrylic acid and then reacting with a polysiloxane having a terminal epoxy group (for example, a compound illustrated by the following structural formula (1), this compound being referred to as polysiloxane FM0521 in the preparation example below). A polysiloxane group can also be introduced by polymerizing the monomer in the form of (meth)acryloyloxyalkylenedialkylchlorosilane and then reacting with a polysiloxane having a terminal epoxy group or a polysiloxane having a terminal modified with an amino group.

Structural formula (1):



The quantity of copolymerization of the polysiloxane group containing unsaturated monomer (b) is in the range of 0.1 to 85% by weight, preferably 0.5 to 70% by weight, more preferably 0.5 to 20% by weight, 20 of the total monomer weight. If the amount is less than 0.1% by weight, the copolymer obtained cannot afford hair an excellent gloss and brilliance or a smooth feeling. If the amount of the monomer exceeds 85% by weight, it will cause problems when it is incorporated into cosmetics or when it is used repeatedly over a long period.

If the monomer represented by the formula (1) described above is monofunctional and the sum of m and n is 80 or more, the copolymerizability of the monomer decreases, so that it is effective to use a bifunctional monomer wherein R₂ is a vinyl group, an acryloyloxy group or a methacryloyloxy group in combination with the monofunctional monomer.

30 Hydrophobic unsaturated monomer (c):

The hydrophobic unsaturated monomer of the component (c) is a hydrophobic unsaturated monomer having radical polymerizability which is used, if necessary, in order to afford the copolymer obtained a hydrophobic property and the strength, hardness and softness of film derived therefrom. The hydrophobic unsaturated monomer has preferably a solubility in water in the range of less than 10 g/100 g in water (25°C).

Examples of the hydrophobic unsaturated monomers include, for example, (a) saturated and unsaturated alkyl (meth)acrylates having 1 to 24 carbon atoms in the alkyl such as methyl (meth)acrylate, allyl (meth)acrylate, isobutyl (meth)acrylate, cyclohexyl (meth)acrylate, octyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, behenyl (meth)acrylate and the like; (b) hydrophobic (meth)acrylates and their derivatives such as butoxyethyl (meth)acrylate, benzyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, ethyleneglycol di(meth)acrylate, 1,3-buteneglycol di(meth)acrylate, diacetonaacrylamide and the like; (c) aromatic unsaturated monomers such as styrene, chlorostyrene, vinyltoluene and the like; and (d) vinyl esters such as vinyl acetate and the like.

45 The amount of the hydrophobic unsaturated monomer polymerized is in the range of 0 to 84.9% by weight to the total monomer weight, and this monomer is not an essential component. If the amount of this monomer exceeds 84.9% by weight, the copolymer thus obtained may have problems that it becomes hardly soluble in water and/or an ethanolic solvent or it is difficult to be removed from hair upon hair washing. The amount of the monomer can be selected at will according to the uses with the upper limit of 50 84.9% by weight. The hydrophilic unsaturated monomer is preferably used in an amount of 40 to 84.5% by weight when the polymer is used as a hair-setting polymer and 0 to 69.5% by weight when the polymer is used as a hair-conditioning polymer.

When a bifunctional unsaturated monomer such as ethyleneglycol di(meth)acrylate, allyl (meth)acrylate or the like is used, it is preferably used in an amount of 2% by weight or less to the total monomer weight.

55

Formation of copolymer

The unsaturated monomers can be copolymerized by well-known radical polymerization methods such as bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization or the like.

Preferred polymerization method is a solution polymerization method, which is conducted by a process comprising dissolving monomers in a solvent, adding a polymerization initiator and stirring under heating the mixture under the nitrogen stream.

the solvent is preferably water and an alcohol such as methanol, ethanol, isopropanol, ethyleneglycol and butylcellosolve. These solvents can be used in combination. The polymerization initiator is preferably a peroxide such as benzoyl peroxide, lauroyl peroxide and an azo compound such as azobisisobutyronitrile or the like.

The monomers concerned are usually used in such a way that all of them in types and amounts are added to the polymerization at once from the initiation of polymerization, but alternatively they can be used in such a way that some of them in types and/or amounts are added to polymerization separately. The solvent is preferably used in such an amount that the copolymer solution obtained has a polymer concentration of 10 to 65% by weight. The amount of the monomers charged may be determined in consideration of factors such as the copolymerizability or the conversion so that the copolymer obtained has a predetermined composition. It goes without saying that the monomers charged has the same composition as that of the copolymer in the case of the conversion of 100%.

The molecular weight of the copolymer can be decided at will by appropriately selecting the polymerization conditions such as polymerization temperature, the kinds and amounts of polymerization initiators, addition methods, the amounts of solvent used, the chain transfer agents when used or the like. In general, the copolymers obtained have preferably the molecular weight in the range of 1,000 to 500,000.

The copolymer can be obtained as a solid by removing the solvent from a copolymer solution, or the solid thus obtained can be diluted with any solvents to obtain a copolymer solution, which are used for further applications. The copolymers thus obtained and the solutions may be used in admixture of the two or more.

[II] Use of the polymer/hair-care products

30

The copolymer thus obtained is preferably used as a polymer suitable for hair-care products in an amount of 0.1 to 10% by weight in well-known compositions such as shampoos, rinses, hair treatment products, hair setting products, cold permanent wave lotions or the like. The hair-care products into which the copolymer is incorporated may be of any forms such as liquid, cream, emulsion, gel or the like. It may also be used in combination with well-known conventional naturally occurring polymers, modified products of naturally occurring polymers or synthetic polymers.

Hair-care products in which the copolymer in accordance with the present invention is used include hair setting compositions for setting hair in desired hair style such as aerosol hair sprays, pump hair sprays, foaming type hair sprayss, hair mists, hair setting lotions, hair styling gels, hair liquids, hair creams, hair oils and the like, and those for providing hair with softness, gloss, smooth combing, recovery from damage, manageability and the like such as shampoos, rinses, hair treatment lotions, cold permanent wave lotions and the like.

More particularly, typical examples of hair-care products in which the copolymers in accordance with the present invention are incorporated are as follows.

(1) Hair-care products for hair setting:

50 Hair-care products for hair setting include those in which water and/or an alcohol e.g. ethanol or isoporanol is used as a solvent known in the art such as aerosol hair spray, pump hair spray, foaming type hair spray, hair mist, hair-setting lotion, hair-styling gel, hair liquid, hair cream, hair oil and the like.

The copolymers in accordance with the present invention are used in these hair-care poroducts as a partial or total substitute for or in combination with anionic, nonionic, cationic and amphoteric polymers and 55 polysiloxne polymers conventionally used in these hair-care products.

The copolymers in accordance with the present invention can also be used in hair-care products in combination with oils or fats, humectants, solubilizing agents, emulsifiers, thickeners, germicides, perfumes and the like conventionally used in hair-care products.

For these uses, it is preferable that the copolymer comprises a unit of the hydrophilic monomer (a) in 15 to 59.5% by weight, a unit of the monomer comprising a polysiloxane group (b) in 0.5 to 45% by weight, and a unit of the hydrophobic monomer (c) in 40 to 84.5% by weight.

When the ionic natures of the hydrophilic monomer (a) are nonionic, anionic, amphoteric in that the monomer has cationic and anionic natures in its molecule, or amphoteric in that a cationic monomer and an anionic monomer are in admixture, it is preferable that a unit of the copolymer comprises the hydrophilic monomer (a) in 20 to 59.5% by weight, a unit of the monomer comprising a polysiloxane group (b) in 0.5 to 40% by weight, and a unit of the hydrophobic monomer (c) in 40 to 79.5% by weight.

When the hydrophilic monomer (a) is cationic, it is preferable that the copolymer comprises a unit of the hydrophilic monomer (a) in 15 to 54.5% by weight, a unit of the monomer comprising a poly siloxane group (b) in 0.5 to 45% by weight, and a unit of the hydrophobic monomer (c) in 40 to 84.5% by weight.

When the hydrophilic monomer (a) is amphoteric in that a cationic monomer and an anionic monomer are in admixture, the ratio by weight of cationic monomer units/anionic monomer units is preferably 1/9 to 9/1.

75

(2) Hair-care products for hair conditioning

Hair-care products for hair conditioning include those in which water and/or an alcohol, e.g. ethanol or isopropanol is used as a solvent such as shampoos, hair rinses, cold permanent wave lotions and the like and those in which water and/or an alcohol e.g. ethanol or isopropanol, or an alcohol and/or a hydrocarbon of a boiling point of 50 to 300 °C such as hair treatment products.

When the hair-care products are shampoos in which the copolymers in accordance with the present invention are used, it is a conventional practice to use in the shampoos anionic, amphoteric or nonionic surfactants, and it is also possible to use in the shampoos foam improves, thickeners, hydrotropes, emulsifiers, conditioning aids, germicides, perfumes and the like.

When the hair-care products are hair-rinses in which the copolymers in accordance with the present invention are used, it is a conventional practice to use in the rinses cationic surfactants, and it is also possible to use in the rinses oils and fats, cationic surfactants, amphoteric surfactants, humectants, solubilizing agents, emulsifiers, thickeners, germicides, hair tonics, perfumes and the like.

When the hair-care products are cold permanent wave lotions, it is a conventional practice to use in the lotions bromates, perborates, oxidation-reduction compositions e.g. thioglycolates or cysteine and the like. It is also possible to use in the lotion surfactants, thickeners, stabilizing agents, emulsifiers, conditioning aids, humectants, germicides, perfumes and the like.

When the hair-care products are hair treatment products, the copolymers in accordance with the present invention are used in these hair treatment products as a partial or total substitute for or in combination with cationic surfactants and/or cationic polymers e.g. cationic polypeptides, cationic celluloses, cationic polysiloxanes and the like. It is also possible to use in the hair treatment products oils and fats, amphoteric polymers, humectants, solubilizing agents, emulsifiers, thickeners, germicides, hair tonics, perfumes and the like.

The copolymers in accordance with the invention when they are used in the hair treatment products are preferably such that the hydrophilic monomer (a) is cationic, amphoteric in that it has cationic and anionic natures in its molecule, or amphoteric in that a cationic monomer and an anionic monomer are in admixture. The hydrophilic monomers (a) may be used singly or in combination, but the ratio by weight of the units of a cationic hydrophilic monomer/the units of an anionic or amphoteric hydrophilic monomer which has anionic and cationic natures in its molecule is 1/9 to 9/1.

The copolymers in accordance with the present invention preferably comprises a unit of the hydrophilic monomer (a) in 30 to 99.5% by weight, a unit of the monomer comprising a polysiloxane group (b) in 0.5 to 70% by weight, and a unit of the hydrophobic monomer in 0 to 69.5% by weight.

50

[III] Examples

The present invention is explained more specifically with reference to the following preparation examples and formulation examples without limit thereto. The parts and percentages in the preparation examples are represented by weight. The parts and percentages in the formulation examples are represented by weight on the basis of effective components.

Preparation Example 1

In a five-neck flask equipped with a reflux condenser, a dropping funnel, a thermometer, a glass tube for nitrogen substitution and a stirrer are charged 70 parts of dimethylaminoethyl methacrylate, 25 parts of 5 N-vinylpyrrolidone, 5 parts of polysiloxane FM0721 and 150 parts of anhydrous ethanol. A 0.6 part amount of azobisisobutyronitrile is added to the mixture, and the polymerization is carried out for 8 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 50% solution in anhydrous alcohol of propanesultone which is equimolar to the dimethylaminoethyl methacrylate is added dropwise from a dropping funnel into the five-neck flask and 10 heated under reflux at 80°C for further 6 hours under a nitrogen stream in order to conduct amphotericization reaction. The polymer thus obtained is referred to as "P-1". In an actual practice, the polymer thus obtained had an average molecular weight of 170,000.

15 Preparation Example 2

In a five-neck flask similar to that in Preparation Example 1 are charged 30 parts of dimethylaminoethyl methacrylate, 70 parts of polysiloxane FM0711 and 200 parts of anhydrous ethanol. One part of 20 azobisisobutyronitrile is added to the mixture, and the polymerization is carried out for 6 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 50% solution in anhydrous ethanol of propanesultone which is equimolar to the dimethylaminoethyl methacrylate is added dropwise from a dropping funnel into the five-neck flask and 25 heated under reflux at 80°C under a nitrogen stream in order to conduct cationization reaction for further 6 hours. The polymer thus obtained is referred to as "P-2". In an actual practice, the polymer obtained had an average molecular weight of 25,000.

Preparation Example 3

30 In a five-neck flask similar to that in Preparation Example 1 are charged 85 parts of dimethylaminoethyl methacrylate, 11 parts of lauryl methacrylate, 3 parts of polysiloxane FM0725, 1 part of polysiloxane FP-2231 and 67 parts of anhydrous ethanol, and the mixture is heated under reflux at 80°C under a nitrogen stream. A solution of 0.6 part of azobisisobutyronitrile in 33 parts of ethanol is added to a five-neck flask by dropping from a dropping funnel over a period of 3 hours. Next, 0.3 part of azobisisobutyronitrile was added 35 to the mixture, and the polymerization is carried out for further 6 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 40% solution in anhydrous ethanol of an aminomethylpropanol neutralization product of monochloracetic acid which is equimolar to the dimethylaminoethyl methacrylate is added dropwise from a dropping funnel into the five-neck flask and heated under reflux at 80°C for further 6 hours under a nitrogen 40 stream in order to conduct amphotericization reaction.

Then, ethanol is removed by heating while pure water is added by from a dropping funnel to the five-neck flask so as to give an aqueous solution of the polymer. The polymer thus obtained is referred to as "P-3". In an actual practice the polymer obtained had an average molecular weight of 300,000.

45

Preparation Example 4

In a five-neck flask similar to that in Preparation Example 1 are charged 40 parts of dimethylaminoethyl methacrylate, 35 parts of t-butyl methacrylate, 24 parts of tridecyl methacrylate, 1 part of polysiloxane 50 FM0721 and 150 parts of anhydrous ethanol. 0.6 part of azobisisobutyronitrile is added, and the polymerization is carried out for 8 hours by heating under reflux at 80°C under a nitrogen stream.

Next, a 40% solution in anhydrous ethanol of a potassium hydroxide neutralization product of monochloracetic acid which is equimolar to the dimethylaminoethyl methacrylate is added dropwise from a dropping funnel into the five-neck flask and heated under reflux at 80°C for further 12 hours under a 55 nitrogen stream in order to conduct amphotericization reaction.

Suspended materials (potassium chloride) are removed by pressurized filtration from the viscous suspension thus obtained.

The filtrate is passed through a column in which a cation exchange resin ("DIAION PK-220", of which

system has been substituted by anhydrous ethanol after regeneration) has been packed and is passed through a column in which an anion exchange resin ("DIAION PA-416", of which system has been substituted by anhydrous ethanol after regeneration) has been packed. The polymer thus obtained is referred to as "P-4". In an actual practice, the polymer obtained had an average molecular weight of
 5 60,000.

Preparation Example 5

10 In a five-neck flask similar to that in Preparation Example 1 are charged 70 parts of N-vinylpyrrolidone, 30 parts of polysiloxane FM0721 and 100 parts of anhydrous ethanol, and 0.6 part of azobisisobutyronitrile is added to the mixture. The polymerization is carried out for 8 hours by heating under reflux at 80 °C under a nitrogen stream.

15 The polymer thus obtained is referred to as "P-5". In an actual practice, the polymer obtained had an average molecular weight of 150,000.

Preparation Example 6

20 In a five-neck flask similar to that in Preparation Example 1 are charged 15 parts of acrylic acid, 5 parts of methacrylic acid, 10 parts of methyl acrylate, 40 parts of butyl methacrylate, 25 parts of lauryl methacrylate, 5 parts of polysiloxane FM0721 and 150 parts of anhydrous ethanol. 0.6 part of benzoyl peroxide is added, and the polymerization is carried out for 6 hours by heating under reflux at 80 °C under a nitrogen stream.

25 Next, a 50% solution in anhydrous ethanol of triethanolamine which corresponds to 85% molar amount of the acid is added dropwise under cooling from a dropping funnel into the five-neck flask. The polymer thus obtained is referred to as "P-4". In an actual practice, the polymer obtained had an average molecular weight of 120,000.

30 Preparation Example 7

In a five-neck flask similar to that in Preparation Example 1 are charged 45 parts of methacrylic acid, 10 parts of methyl methacrylate, 30 parts of iso-butyl methacrylate, 15 parts of palmityl methacrylate and 150 parts of toluene. 0.6 part of benzoyl peroxide is added, and the polymerization is carried out for 6 hours by heating under reflux at 80 °C under a nitrogen stream.

Next, 1 part of benzyltrimethylammonium chloride is added, and 5 parts of polysiloxane FM-0521 is added dropwise from a dropping funnel into the five-neck flask in order to conduct addition reaction by heating under reflux at 80 °C for 6 hours under a nitrogen stream.

40 Toluene in the toluene solution obtained is removed by evaporation by heating to give a precursor polymer as a solid. The polymer is dissolved in a 5% water-containing ethanol so that it has a concentration of 40%.

45 Next, a 50% solution in ethanol (containing 5% of water) of aminomethylpropanol which corresponds to 85% molar amount of the residual acid is added dropwise under cooling from a dropping funnel into the five-neck flask. The polymer thus obtained is referred to as "P-7". In an actual practice, the polymer obtained had an average molecular weight of 90,000.

Formulation Example 1

50 A shampoo composition having the following formulation was prepared.

5

Sodium polyoxyethylenelauryl sulfate (3EO)	16%
Lauroyl diethanolamide	2%
"P-1"	1.5%
Perfume	0.2%
Preservative	0.1%
Coloring matter	trace
Pure water	balance 100%

10

When the composition was used for shampoos, hair after washing was combed smoothly, and the hair after drying had an excellent gloss and brilliance and a smooth feeling so that the hair was combed smoothly.

15 With repeated shampooings, adverse effects such as tackiness were not observed.

Formulation Example 2

20 A shampoo composition having the following formulation was prepared.

25

Sodium polyoxyethylenelauryl sulfate (3EO)	10%
Sodium lauryl sulfate	8%
Lauroyl diethanolamide	2%
"P-3"	1.5%
Pure water	balance 100%

30

When the composition was used for shampoos, excellent effects as in Formulation Example 1 were obtained.

35

Formulation Example 3

A shampoo composition having the following formulation was prepared.

40

Coconut oil fatty acid dimethylaminosulfobetaine	10%
Sodium polyoxyethylenelauryl sulfate (3EO)	5%
"P-5"	0.5%
Pure water	balance 100%

45

When the composition was used for shampoos, excellent effects as in Example 1 was obtained.

50

Formulation Example 4

A rinse composition having the following formulation was prepared.

55

5

Stearyltrimethylammonium chloride	1.5%
Cetanol	2%
"P-2"	0.2%
Perfume	0.2%
Pure water	balance 100%

10 When the composition was used for a rinse, hair after rinsing was combed smoothly, and the hair after drying had an excellent gloss and brilliance and a smooth feeling so that the hair was combed smoothly. With repeated rinsings, adverse effects such as tackiness were not observed.

15 Formulation Example 5

A hair oil composition having the following formulation was prepared.

20

Octamethylcyclotetrasiloxane	40%
"P-2"	8%
Anhydrous ethanol	balance 100%

25

When the composition was used for a rinse, hair after rinsing was combed smoothly, and the hair after drying had an excellent gloss and brilliance and a smooth feeling so that the hair was combed smoothly. When the hair oil composition was applied to hair and the hair was washed in repeated cycle, adverse effects such as tackiness or development of a feeling of physical disorder due to its accumulation were not observed.

Formulation Example 6

35 A diluted polymer solution of the following formulation was charged in a spraying can, which were then charged with a liquefied petroleum gas to prepare a hair spray composition.

40

<u>A diluted polymer solution</u>	
"P-2"	4 parts
Anhydrous ethanol	balance 65 parts
<u>Liquefied petroleum gas</u>	
(3 kg/cm ² G, 20 ° C)	35 parts

45

50 When the composition was used by spraying it onto hair, it afforded the hair an excellent set maintaining capability as well as an excellent gloss and brilliance and a smooth feeling. When the hair oil composition was applied to hair and the hair was washed in repeated cycle, adverse effects such as tackiness or a feeling of physical disorder due to its accumulation were not observed.

55 Formulation Example 7

In the same manner as in Formulation Example 6, a hair spray composition was prepared.

5

<u>A diluted polymer solution</u>	
"P-6"	3 parts
Anhydrous ethanol	balance 70 parts
<u>Liquefied petroleum gas</u>	
(3 kg/cm ² G, 20 ° C)	30 parts

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When the composition was used by spraying it onto hair, an excellent effect like the Example 6 was obtained.

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Formulation Example 8

In the same manner as in Formulation Example 6, a foaming aerosol composition was prepared.

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<u>A diluted polymer solution</u>	
"P-4"	2 parts
YUKAFOMER AM-75R 205S*	2 parts
Polyoxyethylene cetyl ether (10EO)	0.3 parts
Polyoxyethylene cetyl ether (2EO)	0.1 parts
Pure water	balance 88 parts
<u>Liquefied petroleum gas</u>	
(3 kg/cm ² G, 20 ° C)	12 parts

*"YUKAFOMER AM-75R 205S" is a carboxybetaine type amphoteric polymer which is commercially available from MITSUBISHI PETROCHEMICAL CO., LTD.

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When the composition was used by applying it to hair, an excellent effect like the Formulation Example 6 was obtained.

45

Formulation Example 9

A hair set lotion composition having the following formulation was prepared.

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"P-4"	3%
Pure water	60%
Anhydrous ethanol	balance 100%

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When the composition was used by spraying it onto hair, an excellent effect like the Formulation Example 6 was obtained.

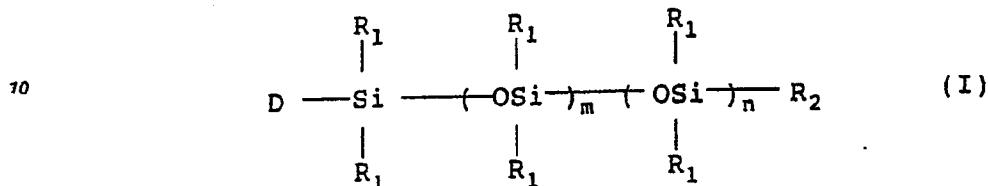
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Claims

1. A polymer for use in hair-care product comprising a copolymer comprising (a) a unit of a hydrophilic

ethylenically unsaturated monomer in a quantity of 15 to 99.9% by weight; (b) a unit of an ethylenically unsaturated monomer having a polysiloxane group in a quantity of 0.1 to 85% by weight; and (c) a unit of a hydrophobic ethylenically unsaturated monomer in a quantity of 0 to 84.9% by weight.

5 2. The polymer for use in hair-care products according to claim 1, wherein the ethylenically unsaturated monomer having a polysiloxane group (b) comprises one or more of the monomers represented by the formula (I):



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wherein D, R₁, R₂, m and n have the following meanings, respectively:

D = an unsaturated group having radical polymerizability selected from the group consisting of a vinyl group, a vinylalkylene group, a vinylhydroxyalkylene group, an acryloyloxyalkylene group and a methacryloyloxyalkylene group;

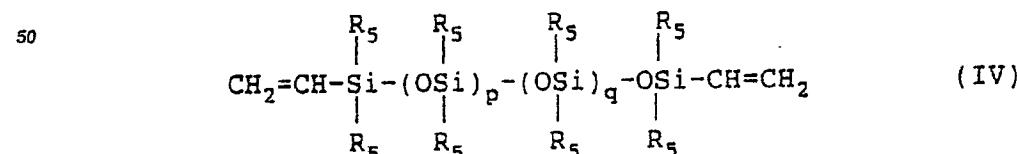
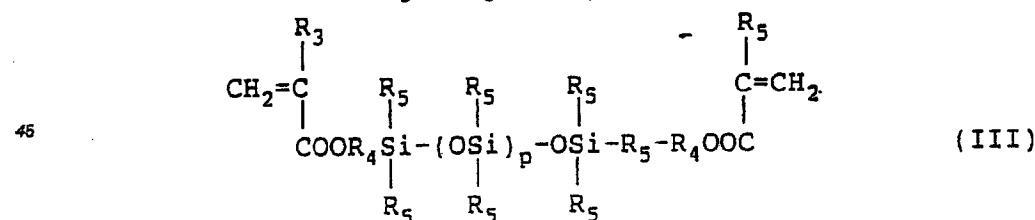
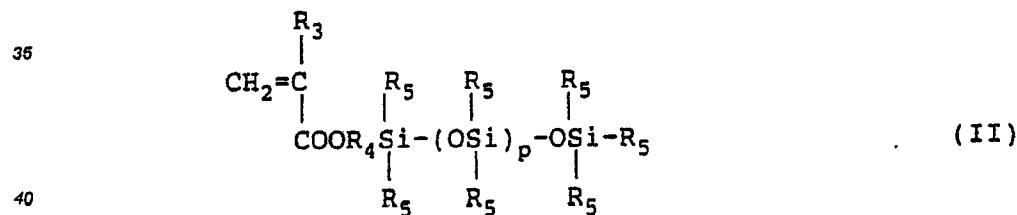
20 R₁ = a hydrogen atom, a phenyl group, an alkyl group having 1 to 10 carbon atoms, a polyalkylene group, a polyoxyalkylene groups of which end has been substituted by an ether or ester group, a polyalkylenepolyamine group, a fatty acid group or a polysiloxane group, respectively;

R² = a hydrogen atom, a phenyl group, an alkyl group having 1 to 10 carbon atoms, a polyalkylene group, a polyoxyalkylene group of which end has been substituted by an ether or ester group, a polyalkylenepolyamine group, a fatty acid group or a polysiloxane group, or an unsaturated group having radical polymerizability selected from the group consisting of a vinyl group, a vinylalkylene group, a vinylhydroxyalkylene group, an acryloyloxyalkylene group or a methacryloyloxyalkylene group;

25 m = an integer from 4 to 150; and

n = an integer from 0 to 150, wherein the sum of m and n is within 150.

30 3. The polymer for use in hair-care products according to claim 1, wherein the ethylenically unsaturated monomer having a polysiloxane group (b) comprises one or a mixture of the two or more of the monomers represented by the formulae (II) to (IV):



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wherein R₃ to R₆, p and q have the following meanings independently of each other between the formulae:
R₃ = a hydrogen atom or a methyl group;

R_4 = an alkylene group having 1 to 4 carbon atoms;
 R_5 = an alkyl group having 1 to 10 carbon atoms or a phenyl group;
 p = an integer of 1 or more; and
 q = an integer of 1 or more, wherein the sum of p and q are within 150.

5 4. The polymer for use in hair-care products according to claim 1, wherein the hydrophilic unsaturated monomer (a) comprises a nonionic unsaturated monomer.

5 5. The polymer for use in hair-care products according to claim 1, wherein the hydrophilic monomer (a) comprise an anionic unsaturated monomer.

10 6. The polymer for use in hair-care products according to claim 1, wherein the hydrophilic monomer (a) comprise a cationic unsaturated monomer.

10 7. The polymer for use in hair-care products according to claim 1, wherein the hydrophilic unsaturated monomer (a) comprise an amphoteric unsaturated monomer in that the monomer has an anionic nature and a cationic nature in its molecule.

15 8. The polymer for use in hair-care products according to claim 1, wherein the hydrophilic unsaturated monomer (a) comprise a mixture of at least two of monomers consisting of a nonionic unsaturated monomer, an anionic unsaturated monomer, a cationic unsaturated monomer, and an amphoteric unsaturated monomer in that the monomer has an anionic nature and a cationic nature in its molecule.

20 9. The polymer for use in hair-care products according to claim 1, wherein the polymer comprises a copolymer comprising (a) a unit of a hydrophilic unsaturated monomer selected from the group consisting of a nonionic monomer, an anionic monomer, an amphoteric monomer in that the monomer has an anionic nature and a cationic nature in its molecule, and a mixture thereof, in a quantity of 20 to 59.5% by weight; (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 40% by weight; and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 40 to 79.5% by weight, the polymer being suitable for use in hair-setting.

25 10. The polymer for use in hair-care products according to claim 1, wherein the polymer comprises a copolymer comprising (a) a unit of a hydrophilic monomer which is a mixture of a cationic unsaturated monomer and an anionic unsaturated monomer, the weight ratio of the cationic monomer to the anionic monomer being 1/9 to 9/1, in a quantity of 20 to 59.5% by weight, (b) a unit of the unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 40% by weight; and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 40 to 79.5% by weight, the polymer being suitable for hair setting.

30 11. The polymer for use in hair-care products according to claim 1, wherein the polymer comprises a copolymer comprising (a) a unit of a hydrophilic unsaturated monomer which is cationic, in a quantity of 15 to 54.5% by weight; (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 45% by weight; and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 40 to 84.5% by weight, the polymer being suitable for hair setting.

35 12. The polymer for use in hair-care products according to claim 1, wherein the polymer comprises a copolymer comprising (a) a unit of a hydrophilic unsaturated monomer, in a quantity of 15 to 99.5% by weight, (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 20% by weight and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 0 to 84.5% by weight.

40 13. The polymer for use in hair-care products according to claim 1, wherein the polymer comprises a copolymer comprising (a) a unit of a hydrophilic unsaturated monomer which is a cationic monomer or an amphoteric monomer in that the monomer has an anionic nature and a cationic nature in its molecule, in a quantity of 30 to 99.5% by weight; (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 70% by weight; and (c) a unit of a hydrophobic unsaturated monomer, in a quantity of 0 to 69.5% by weight, the polymer being suitable for hair conditioning.

45 14. The polymer for use in hair-care products according to claim 1, wherein the polymer comprises a copolymer comprising (a) a unit of a hydrophilic monomer which is a combination of a cationic monomer and an anionic monomer or which is a combination of a cationic monomer and an amphoteric monomer in that the monomer has a anionic nature and a cationic nature in its molecule, the weight ratio of the cationic monomer to the anionic monomer or to the amphoteric monomer being 1/9 to 9/1, in a quantity of 30 to 99.5% by weight; (b) a unit of an unsaturated monomer having a polysiloxane group, in a quantity of 0.5 to 70% by weight; and (c) a unit of hydrophobic unsaturated monomer, in a quantity of 0 to 69.5% by weight, the polymer being suitable for hair conditioning.

50 15. A hair-care product comprising the polymer as claimed in claim 1 dissolved in water and/or an alcohol in a concentration of 0.5 to 10% by weight.

55 16. A hair-care product comprising the polymer as claimed in claim 1 dissolved in a concentration of 0.5 to 10% by weight in a hydrocarbon of a boiling temperature of 50 to 300 °C or in a mixture of the hydrocarbon with an alcohol.



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(57) Hair conditioning and styling compositions.

(57) Hair care compositions which provide improved styling and hair conditioning properties are disclosed. The compositions comprise from about 0.1% to about 10.0% of a specifically-defined silicone copolymer and from about 0.5% to about 99.5% of a carrier suitable for application to hair. These compositions are characterized by the fact that, when dried, the polymer phase separates into a discontinuous phase which includes a silicone macromer and a continuous phase which includes the copolymer backbone.

EP 0 412 704 A2

HAIR CONDITIONING AND STYLING COMPOSITIONS

TECHNICAL FIELD

This application is a continuation-in-part of U.S. Application Serial No. 390,568, Bolich and Torgerson, filed August 7, 1989.

The present invention relates to hair care compositions which have improved hair conditioning and style retention properties while still leaving the hair with a natural non-sticky feel. These compositions utilize a group of specific silicone macromer-containing copolymers.

10

BACKGROUND OF THE INVENTION

The desire to have hair retain a particular shape is widely held. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of mousse, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following , shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

It has now been discovered that hair care compositions comprising certain specifically-defined silicone macromer-containing copolymers provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays, tonics, lotions, gels, and mousse. The compositions provide these benefits to hair without leaving the hair with a stiff or sticky/tacky feel and without negatively affecting dry hair properties, such as ease of combing. Further, hair to which the compositions of the present invention have been applied may be restyled several times without requiring reapplication of the compositions.

The results are surprising since other materials which have been typically used in hair care compositions to provide style retention, such as resins and gums, generally hurt dry hair properties (e.g., combing) and leave hair with a sticky and/or stiff feel. Furthermore, silicone materials typically used for hair conditioning tend to hurt style retention.

Siloxanes (see, for example, U.S. Patent 3,208,911, Oppiger, issued September 28, 1965) and siloxane-containing polymers have been taught for use in hair conditioning compositions. U.S. Patent 4,601,902, Fridd et al., issued July 22, 1986, describes hair conditioning or shampoo/conditioner compositions which include a polydiorganosiloxane having quaternary ammonium substituted groups attached to the silicon, and a polydiorganosiloxane having silicon-bonded substituents which are amino-substituted hydrocarbon groups. U.S. Patent 4,654,161, Kollmeier et al., issued March 31, 1987, describes a group of organopolysiloxanes containing betaine substituents. When used in hair care compositions, these compounds are said to provide good conditioning, compatibility with anionic components, hair substantivity, and low skin irritation. U.S. Patent 4,563,347, Starch, issued January 7, 1986, relates to hair conditioning compositions which include siloxane components containing substituents to provide attachment to hair. Japanese Published Application 56-129,300, Lion Corporation, published October 9, 1981, relates to shampoo conditioner compositions which include an organopolysiloxane oxyalkylene copolymer together with an acrylic resin. U.S. Patent 4,479,893, Hirota et al., issued October 30, 1984, describes shampoo conditioner compositions containing a phosphate ester surfactant and a silicon derivative (e.g., polyether- or alcohol-modified siloxanes). Polyether-modified polysiloxanes are also disclosed for use in shampoos in U.S. Patent 3,957,970, Korkis, issued May 18, 1976. U.S. Patent 4,185,087, Moriino, issued January 22, 1980, describes quaternary nitrogen derivatives of trialkylamino hydroxy organosilicon compounds which are said to have superior hair conditioning properties.

Siloxane-derived materials have also been used in hair styling compositions. Japanese Published Application 56-092,811, Lion Corporation, published December 27, 1979, describes hair setting composi-

tions which comprise an amphoteric acrylic resin, a polyoxyalkylene-denatured organopolysiloxane, and polyethylene glycol. U.S. Patent 4,744,978, Homan et al., issued May 17, 1988, describes hair styling compositions (such as hair sprays) which include the combination of a carboxyfunctional polydimethylsiloxane and a cationic organic polymer containing amine or ammonium groups. Hair styling compositions which

5 include polydiorganosiloxanes and a cationic organic polymer are taught in U.S. Patent 4,733,677, Gee et al., issued March 29, 1988, and U.S. Patent 4,724,851, Cornwall et al., issued February 16, 1988. Finally, European Patent Application 117,360, Cantrell et al., published September 5, 1984, discloses compositions, containing a siloxane polymer having at least one nitrogen-hydrogen bond, a surfactant, and a solubilized titanate, zirconate or germanate, which act as both a conditioner and a hair styling aid.

10 Siloxane-containing polymers have also been used in non-hair care applications. U.S. Patent 4,136,250, Mueller et al., issued January 23, 1979, relates to polymeric materials used in biological contexts where oxygen permeable and tissue compatible membranes are required. They can also be used as carriers for biologically-active substances. These materials are hydrophilic water-insoluble gels which include a low molecular weight terminal olefinic siloxane macromer and a polymer containing water-soluble monoolefinic

15 monomer. U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, describes pressure sensitive adhesive compositions which include a copolymer with a vinyl polymeric backbone having grafted thereto polysiloxane moieties. U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, relates to adhesive release coating compositions which comprise polysiloxane-grafted copolymers and blends of those copolymers with other polymeric materials. None of these last three patents suggest the use of the

20 disclosed siloxane-containing polymers in hair care compositions.

It is an object of the present invention to formulate hair care compositions which provide effective hair conditioning and style retention properties.

It is also an object of the present invention to formulate hair care compositions which provide conditioning and style retention from a single composition.

25 It is a further object of the present invention to formulate hair care compositions which provide good style retention without leaving hair with a stiff or sticky/tacky feel.

It is a further object of the present invention to provide an improved method for styling and conditioning hair.

These and other objects will become readily apparent from the detailed description which follows.

30 Unless otherwise indicated, all percentages and ratios herein are by weight.

SUMMARY OF THE INVENTION

35 The present invention relates to hair care compositions comprising

(a) from about 0.1% to about 10.0% of a copolymer, having a molecular weight of from about 10,000 to about 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer comprising C monomers and components selected from the group

40 consisting of A monomers, B monomers, and mixtures thereof wherein:

A is at least one free radically polymerizable vinyl monomer, the amount by weight of A monomer, when used, being up to about 98% of the total weight of all monomers in said copolymer;

B is at least one reinforcing monomer copolymerizable with A, the amount by weight of B monomer, when used, being up to about 98% of the total weight of all monomers in said copolymer, said B monomer being selected from the group consisting of polar monomers and macromers, preferably having a Tg or a Tm above about -20°C; and

45 C is a polymeric monomer having a molecular weight of from about 1,000 to about 50,000 and the general formula

$X(Y)_nSi(R)_{3-m}(Z)_m$ wherein

50 X is a vinyl group copolymerizable with the A and B monomers

Y is a divalent linking group

R is a hydrogen, lower alkyl, aryl or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after copolymerization

55 n is 0 or 1

m is an integer from 1 to 3

wherein C comprises from about 0.01% to about 50% of the copolymer;

(b) from about 0.5% to about 99.5% of a carrier suitable for application to hair.

In another embodiment, the hair care compositions of the present invention include specifically-defined phase separating copolymers of silicone with a non-silicone adhesive polymer, preferably these compositions comprise

- 5 (a) from about 0.1% to about 10.0% of a silicone-containing copolymer having a vinyl polymeric backbone, preferably having a Tg above about -20 °C, and having grafted to the backbone a polydimethylsiloxane macromer having a weight average molecular weight between about 1,000 and about 50,000; and
- 10 (b) from about 0.5% to about 99.5% of a carrier suitable for application to hair;
- 15 the polymer and carrier selected such that, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone.

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DETAILED DESCRIPTION OF THE INVENTION

The essential, as well as the optional, components of the present invention are described below.

20

Silicone-Containing Copolymer

The compositions of the present invention contain from about 0.1% to about 10.0%, preferably from about 0.5% to about 8.0%, of specifically-defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers should have a weight average molecular weight of from about 10,000 to about 1,000,000 (preferably from about 30,000 to about 300,000) and, preferably, have a Tg of at least about -20 °C. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone, and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

In its broadest sense, the polymers useful in the hair care compositions of the present invention include all properly defined copolymers of silicone with a non-silicone adhesive polymer. To be useful such copolymers should satisfy the following four criteria:

- 35 (1) when dried the copolymer phase-separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion;
- (2) the silicone portion is covalently attached to the non-silicone portion;
- (3) the molecular weight of the silicone portion is from about 1,000 to about 30,000; and
- 40 (4) the non-silicone portion must render the entire copolymer soluble or dispersible in the hair care composition vehicle and permit the copolymer to deposit on hair. In addition to the graft copolymers described above, useful copolymers include block copolymers containing up to about 50% (preferably from about 10% to about 20%) by weight of one or more polydimethyl siloxane blocks and one or more non-silicone blocks (preferably acrylates or vinyls).

The most preferred polymers comprise a vinyl polymeric backbone, preferably having a Tg or a Tm above about -20 °C and, grafted to the backbone, a polydimethylsiloxane macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron micrography. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of

Virginia, 1987, and references cited therein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface which is entirely covered by silicone even when the concentration of the silicone by weight in the whole polymer is low (2% to 20%). This is demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

10 Examples of useful copolymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. These copolymers are comprised of monomers A, C and, optionally, B, which are defined as follows. A is at least one free radically polymerizable vinyl monomer or monomers. B, when used, comprises at least one reinforcing monomer copolymerizable with A and is selected from the group consisting of polar monomers and macromers having a Tg or a Tm above about -20°C. When used, B may be up to about 98%, preferably up to about 80%, more preferably up to about 20%, of the total monomers in the copolymer. Monomer C comprises from about 0.01% to about 50.0% of the total monomers in the copolymer.

20 Representative examples of A (hydrophobic) monomers are acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, 30 isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, and mixtures thereof.

35 Representative examples of B monomers (hydrophilic) include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization) vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl 40 methacrylate, vinyl pyrrolidone, and mixtures thereof.

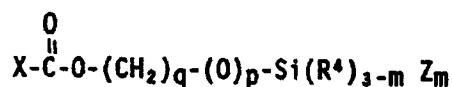
The C monomer has the general formula



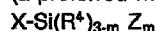
wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, lower alkyl, aryl or alkoxy; Z is a monovalent siloxane polymeric moiety having a number 45 average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions and is pendant from the vinyl polymeric backbone, described above; n is 0 or 1; and m is an integer from 1 to 3. C has a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably from about 10,000 to about 20,000. Preferably, the C monomer has a formula selected from the following group:

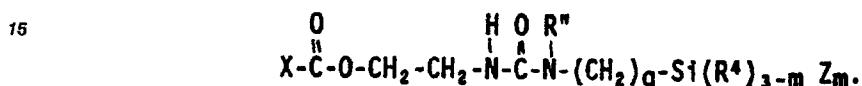
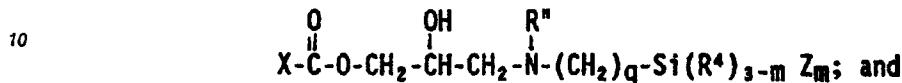
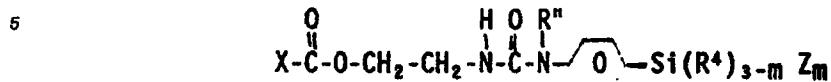
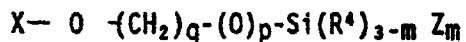
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(a preferred monomer, particularly preferred when p = 0 and q = 3)





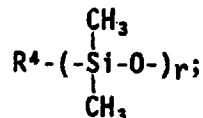
In those structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R⁴ is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; x is

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R¹ is hydrogen or -COOH (preferably R¹ is hydrogen); R² is hydrogen, methyl or -CH₂COOH (preferably R² is methyl); Z is

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R⁴ is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R⁴ is alkyl); and r is an integer from about 5 to about 700 (preferably r is about 250).

40

The polymers of the present invention generally comprise from 0% to about 98% (preferably from about 5% to about 98%, more preferably from about 50% to about 90%) of monomer A, from about 0% to about 98% (preferably from about 7.5% to about 80%) of monomer B, and from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of monomer C. The combination of the A and B monomers preferably comprises from about 50.0% to about 99.9% (more preferably about 60% to about 99%, most preferably from about 75% to about 95%) of the polymer. The composition of any particular copolymer will help determine its formulation properties. In fact, by appropriate selection and combination of particular A, B and C components, the copolymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous formulation preferably have the composition: from about 0% to about 70% (preferably from about 5% to about 70%) monomer A, from about 30% to about 98% (preferably from about 30% to about 80%) monomer B, and from about 1% to about 40% monomer C. Polymers which are dispersible have the preferred composition: from about 0% to about 70% (more preferably from about 5% to about 70%) monomer A, from about 20% to about 80% (more preferably from about 20% to about 60%) monomer B, and from about 1% to about 40% monomer C.

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In one aspect of the present invention, the polymers comprise from about 5% to about 98% A monomer, from about 0.01% to about 50% C monomer, and from 0% to about 98% B monomer. In these polymers, it is preferred that A be selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, since such polymers can be dissolved directly in cyclomethicone solvents without requiring co-solvents. This is surprising in view of U.S. Patents 4,693,935 (Mazurek) and 4,728,571 (Clemens et al), which suggest that tertiary alcohols are not suitable A monomers.

Particularly preferred polymers for use in the present invention include the following (the weight percents below refer to the amount of reactants added in the polymerization reaction, not necessarily the amount in the finished polymer):

- acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer-20,000 molecular weight)
5 (10/70/20 w/w/w) (I)
- N,N-dimethylacrylamide/isobutyl methacrylate/(PDMS macromer -20,000 molecular weight) (20/60/20 w/w/w) (II)
- N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/(PDMS macromer - 10,000 molecular weight) (10.5/56/3.5/30 w/w/w/w) (III)
- 10 N,N-dimethylacrylamide/(PDMS macromer - 20,000 molecular wt) (80/20 w/w) (IV)
- t-butylacrylate/t-butyl methacrylate/(PDMS macromer - 10,000 molecular wt) (56/24/20 w/w/w) (V)
- t-butylacrylate/(PDMS macromer-10,000 molecular wt) (80/20 w/w) (VI)
- t-butylacrylate/N,N-dimethylacrylamide/(PDMS macromer -10,000 molecular weight) (70/10/20) (VII)
- t-butylacrylate/acrylic acid/(PDMS monomer -10,000 molecular weight) (75/5/20) (VIII)

15 The silicone-containing copolymers described above are synthesized as follows.

The polymers are synthesized by free radical polymerization methods, the general principles of which are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is reasonable. Typical 20 monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired. The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically 25 from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified, as needed.

By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction 30 loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

Polymer I: Place 10 parts acrylic acid, 70 parts n-butyl-methacrylate, and 20 parts 20K PDMS macromer 35 in a flask. Add sufficient ethyl acetate to produce a final monomer concentration of 40%. Add initiator, benzoyl peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60 °C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the ethyl acetate by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts Isobutylmethacrylate, and 20 parts silicone 40 macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62 °C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Maintain temperature at 62 °C, with a sufficient rate of argon flow to keep the solution mixed. Monitor the reaction visually, ensuring that 45 no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

Polymer III: Place 10.5 parts N,N-dimethylmethacrylamide, 56 parts Isobutyl methacrylate, 3.5 parts 2-ethylhexylmethacrylate, and 30 parts 10K PDMS macromer in a reaction vessel fitted with an argon 50 sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene or isopropanol to bring the final monomer concentration to 20% by weight. Begin stirring and sparge with argon for 1 hour. While sparging, heat to 60 °C in a water bath. Add Initiator, azobisisobutyronitrile, to a level of 0.25% (if toluene is the solvent) or 0.125% (if isopropanol is the solvent) by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60 °C. Allow to react for 6 hours. Terminate the reaction and remove the solvent as with Polymer II.

The compositions of the invention also comprise a carrier, or a mixture of such carriers, which are suitable for application to hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, most preferably from about 10.0% to about 90.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate solvent will also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on hair (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone copolymer being used. The nature and proportion of B monomer in the copolymer largely determines its polarity and solubility characteristics. The silicone copolymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (such as ethanol, isopropanol), hydro-alcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane), and mixtures thereof. Preferred solvents include water, ethanol, volatile silicon derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or immiscible with each other.

Where the hair care compositions are conditioner compositions, the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkytrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The vehicles may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), Incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarín, et al., issued May 26, 1981; British Specification 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.05% to about 5.0% of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Preferred vehicles for use in the compositions of the present invention include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA). These vehicles are described in detail in the following three concurrently-filed patent applications: Vehicle Systems for Use In Hair Care Compositions, Bolich, Norton and Russell, docket numbers 4000, 4001 and 4002, incorporated herein by reference.

Other carriers, suitable for use with the present invention are, for example, those used in the formulation

of tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also require an emulsifying agent to keep the silicone copolymer

5 homogeneously dispersed in solution. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. If such an emulsifying agent is used, it is present at a level of from about 0.25% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

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Optional Ingredients

15 The hair care compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

20

Surfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly, shampoo and conditioner compositions. When present, the surfactant comprises from about 0.05% to about 50% of 25 the composition. For a shampoo, the level is preferably from about 10% to about 30%, most preferably from about 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

30 Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from about 10 to about 20 carbon atoms. Preferably, R has from about 12 to about 18 carbon atoms in both the alkyl 35 and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with about 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

40 Specific examples of alkyl ether sulfates which may be used in the present invention are sodium coconut alkyl triethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide. 45 Such a mixture also comprises from about 0 to about 20% by weight C_{12-13} compounds; from about 60 to about 100% by weight of $\text{C}_{14-15-15}$ compounds, from about 0 to about 20% by weight of $\text{C}_{17-18-19}$ compounds; from about 3 to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to about 90% by weight of compounds having a degree of ethoxylation of from about 1 to about 4; from about 10 to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to 50 about 8; and from about 0.1 to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



55 wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having about 8 to about 24 carbon atoms,

preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12-18} n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diethyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , etc., when used in the gaseous form.

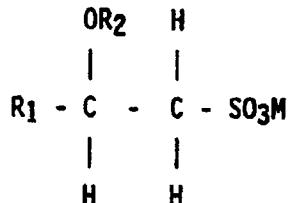
The α -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific α -olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, Pflaumer and Kessler, issued July 25, 1967, incorporated herein by reference.

Another class of anionic organic surfactants are the β -alkyloxy alkane sulfonates. These compounds have the following formula:

35



where R_1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R_2 is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

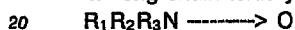
Specific examples of β -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein include: potassium- β -methoxydecanesulfonate, sodium 2-methoxy-tridecanesulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecylsulfonate, sodium β -methyoxyoctadecylsulfonate, and ammonium β -n-propoxydodecylsulfonate.

Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's, Detergents and Emulsifiers, 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl

aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.
- 10 2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000, are satisfactory.
- 15 3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.
4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecylidiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyldimethylamine oxide, 3-dodecoxy-2-hydroxypropyl(3-hydroxy propyl)amine oxide, dimethylhexadecylamine oxide.

- 30 5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxaoctadecylidimethyl phosphine oxide, cetyltrimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyl(2-hydroxyethyl) phosphine oxide, stearyltrimethylphosphine oxide, cetylethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldihydroxymethylphosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

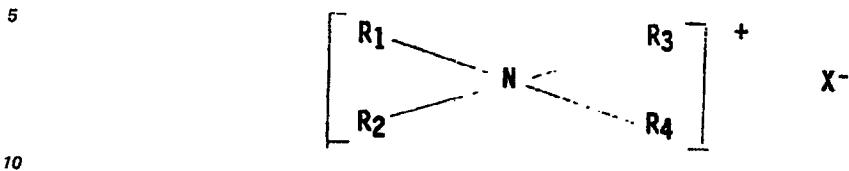
- 40 6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

60 Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's. Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591,

55 Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from

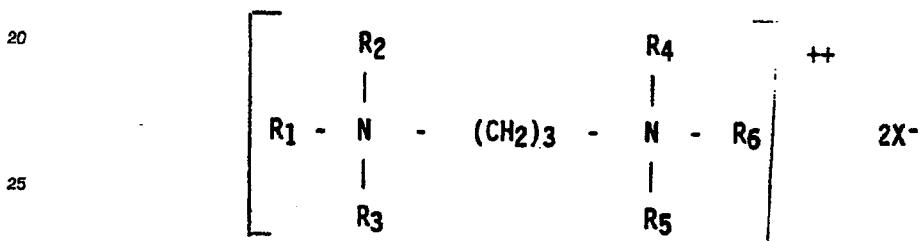
about 0.05% to about 5%.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R₁-R₄ are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups.

Other quaternary ammonium salts useful herein have the formula:



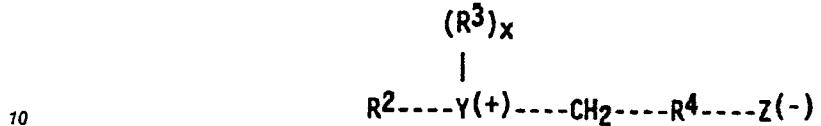
30 wherein R₁ is an aliphatic group having from about 16 to about 22 carbon atoms, R₂, R₃, R₄, R₅, and R₆ are selected from hydrogen and alkyl having from about 1 to about 4 carbon atoms, and X is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R₁ and R₂ have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dicicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

50 Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbenzylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, incorporated by reference herein.

55 Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can

be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these 6 compounds is:



wherein R² contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glycercyl moiety; Y is selected from the 15 group consisting of nitrogen, phosphorus, and sulfur atoms; R³ is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R⁴ is an alkylene or hydroxylalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

20 Examples of such surfactants include:

- 4-[N-N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecoxylphosphonio]2-hydroxy-propane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 25 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 30 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gammacarboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha carboxyethyl betaine. 35 The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the RCONH(CH₂)₃ radical is attached to the nitrogen atom of the betaine are also useful in this invention.

40 Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the 45 one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

The above-mentioned surfactants can be used alone or in combination in the hair care compositions of 50 the present invention. The alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof are preferred for use herein.

The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, 55 e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonoethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as

cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, and sodium carbonate; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; 5 sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

The pH of the present compositions should be between about 3 and about 9, preferably between about 4 and about 8.

10 As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Methods of making various types of hair care compositions are described more specifically in the following examples.

15

Method of Use

20 The hair care compositions of the present invention are used in conventional ways to provide the hair conditioning/styling/ hold benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair, which may then be rinsed from the hair (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, and tonic products). By "effective amount" is meant an amount sufficient to provide the hair conditioning/styling/hold benefits desired 25 considering the length and texture of the hair, and the type of product used. Preferably, the product is applied to wet or damp hair prior to drying and styling of the hair. After the compositions of the present invention are applied to the hair, the hair is dried and styled in the usual ways of the user.

25 The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

The following table defines the silicone copolymers used in the examples (weight ratios given refer to proportion added to reaction mix):

35 Copolymer #1 10/70/20 acrylic acid/n-butylmethacrylate/silicone macromer S2, polymer molecular weight about 100,000
 Copolymer #2 10/70/20 dimethylacrylamide/isobutyl methacrylate/silicone macromer S2, polymer molecular weight about 400,000
 Copolymer #3 60/20/20 diallyldimethyl ammonium chloride/isobutyl methacrylate/silicone macromer S1, 40 polymer molecular weight about 500,000
 Copolymer #4 40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, polymer molecular weight about 400,000
 Copolymer #5 10/70/20 acrylic acid/n-butyl methacrylate/silicone macromer S1, polymer molecular weight about 300,000
 45 Copolymer #6 25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, polymer molecular weight about 200,000
 Copolymer #7 60/25/15 N,N-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, polymer molecular weight about 200,000
 Copolymer #8 12/64/4/20 N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS 50 macromer S1, polymer molecular weight about 300,000
 Copolymer #9 30/40/10/20 dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
 Copolymer #10 80/20 t-butylacrylate/PDMS macromer S2, polymer molecular weight about 150,000
 Silicone macromer S1- has a molecular weight of about 20,000 and is prepared in a manner similar to 55 Example C-2c of U.S. Patent 4,728,571, Clemens, issued March 1, 1988.
 Silicone macromer S2- has a molecular weight of about 10,000 and is prepared in a manner similar to Example C-2b of U.S. Patent 4,728,571, Clemens, issued March 1, 1988.

EXAMPLE I

The following is a hair spray composition representative of the present invention.

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Component	Weight %
Silicone Copolymer #4	2.00
Ethanol	72.90
Perfume	0.10
Isobutane propellant	25.00

15 This product is prepared by adding the silicone copolymer and perfume to the ethanol and mixing for several hours until all the polymer is dissolved. This "concentrate" is then placed in aerosol cans which are fitted with valves crimped under vacuum and then filled through the valve stem with Isobutane dispensed by a pressure filler.

20

EXAMPLE II

The following is a shampoo composition representative of the present invention.

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Component	Weight %
Styling Agent	
Silicone Copolymer #2	1.00
Chloropropyl heptamethyl cyclotetrasiloxane	3.00
Premix	
Silicone gum	0.50
Dimethicone, 350 cs. fluid	0.50
Main Mix	
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan gum	1.20
Kathon CG ¹	0.04
Citric acid to pH 4.5	q.s.
Double reverse osmosis (DRO) H ₂ O	q.s.

¹ preservative commercially available from Rohm & Haas

50 The Styling Agent and Premix are blended separately in a conventional manner. The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150° F with agitation for 1/2 hour. The Styling Agent and Premix are then added sequentially with about ten minutes agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation.

55

EXAMPLE III

The following is a shampoo composition representative of the present invention.

Component	Weight %
Ammonium lauryl sulfate	7.00
Ammonium laureth sulfate	7.00
Cocamide MEA	2.50
Silicone Copolymer #3	1.00
Natrosol 250H ¹	1.00
Glydant ²	0.37
DRO H ₂ O	q.s.

¹ hydroxyethyl cellulose commercially available from Aqualon Co.

² preservative commercially available from Glyco, Inc.

15

The shampoo is made by first dispersing the Natrosol and silicone copolymer in the water for about 1 hour with conventional agitation. The remaining ingredients are then added.

20

EXAMPLE IV

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Component	Weight %
Styling Agent Premix	
Silicone Copolymer #8	2.00
Phenethylpentamethyl disiloxane	6.00
Octamethyl cyclotetrasiloxane	3.00
Xanthan Premix	
Xanthan gum	0.25
DRO H ₂ O	25.00
Main Mix	
Dihydrogenated tallow-dimethylammonium chloride (DTDMAC)	0.50
EDTA, disodium salt	0.10
D.C. 929 ¹	2.00
Perfume	0.10
Poly Surf C ²	0.75
Locust bean gum	0.75
Kathon CG ³	0.04
DRO H ₂ O	q.s.

¹ amodimethicone, commercially available from Dow Corning

² hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.

50

³ preservative commercially available from Rohm and Haas

55

The Styling Agent and Xanthan Premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating with agitation to 95°C for about 1/2 hour. As the batch is cooled, the Styling Agent and Xanthan Premixes are added at about 60°C with vigorous mixing. The batch is then cooled to ambient temperature.

EXAMPLE V

The following is a styling rinse composition representative of the present invention.

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Component	Weight %
Premix A	
Silicone Copolymer #3	2.00
DRO H ₂ O	10.00
Premix B	
Silicone Copolymer #4	2.00
DRO H ₂ O	15.00
NaOH solution (50%)	0.20
Main Mix	
Poly Surf C ¹	1.00
Stearamide DEA	0.50
Ethanol	10.00
Perfume	0.20
DRO H ₂ O	q.s.

¹ hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.

Both premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating to about 60°C with mixing. The premixes are then added to the Main Mix with agitation for about 1/2 hour and the batch is cooled to ambient temperature. Either sodium hydroxide or citric acid, if necessary, is added to adjust composition to pH 6.5.

35

EXAMPLE VI

The following is a hair grooming tonic composition representative of the present invention.

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Component	Weight %
Silicone Copolymer #9	0.70
Perfume	0.10
Ethanol	q.s.

The composition is made by mixing the above components together in a conventional manner.

50

EXAMPLE VII

The following is a shampoo composition representative of the present invention.

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Component	Weight %
Ammonium laureth sulfate	7.00
Cocamido propyl betaine	6.00
Silicone Copolymer #6	2.00
Ethanol	10.00
PEG 150 distearate	2.00
Glydant ¹	0.38
Perfume	1.00
DRO H ₂ O	q.s.

¹ preservative commercially available from Glyco, Inc.

15 The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70 °C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. Composition pH is adjusted to 6.3 by the addition of citric acid or sodium hydroxide, if necessary.

20

EXAMPLE VIII

25 The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #5	3.00
Phenylpentamethyl disiloxane	9.00
<u>Premix</u>	
Silicone gum GE SE76 ¹	0.50
Decamethyl cyclopentasiloxane	4.00
<u>Main Mix</u>	
Poly Surf C ²	0.60
Locust bean gum	0.50
EDTA, disodium salt	0.15
DTDMAC	0.65
Glydant ³	0.40
DRO H ₂ O	q.s.

45 ¹ Commercially available from General Electric

² hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

³ preservative commercially available from Glyco, Inc.

60

The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95 °C for 1/2 hour with agitation. As the batch is cooled to about 60 °C, the Premix and Styling Agent mix are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

55

EXAMPLE IX

The following is a styling rinse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
5	<u>Styling Agent</u>	
	Silicone Copolymer #10 Octamethyl cyclotetrasiloxane	3.00 9.00
	<u>Premix</u>	
10	Silicone gum GE SE 76 ¹ Decamethyl cyclopentasiloxane	0.50 4.00
	<u>Main Mix</u>	
15	Poly Surf C ² Stearamide DEA DTDMAC Kathon CG ³ Imidazole Perfume DRO H ₂ O	1.25 0.40 0.50 0.03 0.15 0.10 q.s.
20		
25		

¹ Commercially available from General Electric

² hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

³ preservative commercially available from Rohm & Haas

30 The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95 °C for 1/2 hour with agitation. As the batch is cooled to about 60 °C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

EXAMPLE X

The following is a cold-wave hair perm composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
40	Thioglycolic acid Monoethanolamine Silicone Copolymer #3 PEG 10 monostearate DRO H ₂ O	5.00 6.00 1.50 0.50 q.s.
45		

50 The composition is prepared by blending all the ingredients with agitation for about 1/2 hour at 60 °C and then cooling to ambient temperature.

EXAMPLE XI

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The following is a hair conditioner composition representative of the present invention.

Component	Weight %
<u>Styling Agent Premix</u>	
Silicone Copolymer #9 Phenyl pentamethyl disiloxane	1.00 4.00
<u>Silicone Premix</u>	
Silicone gum, GE SE76 ¹ Octamethyl cyclotetrasiloxane	0.30 1.70
<u>Main Mix</u>	
Cetyl alcohol	1.00
Quaternium 18 ²	0.85
Stearyl alcohol	0.70
Natrosol 250 MBR ³	0.50
Ceteareth-20	0.35
Fragrance	0.20
Dimethicone copolyol	0.20
Citric acid	0.13
Methylchloroisothiazolinone, methylisothiazolinone	0.04
Sodium chloride	0.01
DRO H ₂ O	q.s.

¹ Commercially available from General Electric

² Diallyl quaternary ammonium compound, commercially available from Sherex

³ hydroxyethyl cellulose material, commercially available from Aqualon Co.

³⁰ The product is prepared by comixing all the Main Mix ingredients, heating to about 60 °C with mixing, and colloid milling down to about 45 °C. At this temperature, the two premixes are added separately with moderate agitation and the batch allowed to cool to ambient temperature.

³⁵

EXAMPLE XII

The following is a styling gel composition representative of the present invention.

⁴⁰

Component	Weight %
Silicone Copolymer #7	2.00
Carbopol 940 ¹	0.75
Triethanolamine	1.00
Dye solution	0.05
Perfume	0.10
Laureth-23	0.10
DRO H ₂ O	q.s.

⁶⁰

¹ cross-linked polyacrylic acid, commercially available from B. F. Goodrich

⁵⁵

This batch is made by mixing the listed components together in a conventional manner.

EXAMPLE XIII

The following is a hair mousse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
5	Silicone Copolymer #7	3.00
	Ethanol	15.00
	Cocamine oxide	0.60
	D.C. 190 ¹	0.20
10	Cocamide DEA	0.30
	Perfume	0.10
	Isobutane	7.00
	DRO H ₂ O	q.s.

¹ dimethicone copolyol, commercially available from Dow Corning

15

The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

20

EXAMPLE XIV

25 The following is a pump hair spray composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
30	Silicone Copolymer #1	2.50
	Dibutyl phthalate	0.20
	Phenyltrimethicone	0.30
	Perfume	0.05
	Aminomethyl propanol	0.20
35	Ethanol	q.s.

This composition is made by mixing the listed components together in a conventional manner.

When the compositions defined in Examples I-XIV are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

Claims

- 45 1. A hair care composition characterized in that it comprises:
 - (a) from 0.1% to 10.0% of a 'copolymer, having a molecular weight of from 10,000 to 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer comprising C monomers and components selected from A monomers, B monomers, and mixtures thereof, wherein:
- 50 A is at least one free radically polymerizable vinyl monomer, preferably selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, the amount by weight of A monomer, when used, being up to about 98% by weight of the total weight of all monomers in said copolymer;
- B is at least one reinforcing monomer copolymerizable with A, the amount by weight of B monomer, when used, being up to about 98% of the total weight of all monomers in said copolymer, said B monomer being selected from polar monomers and macromers; and
- 55 C is a polymeric monomer having a molecular weight of from 1,000 to 50,000 and the general formula X(Y)_nSi(R)_{3-m}(Z)_m wherein
- X is a vinyl group copolymerizable with the A and B monomers
- Y is a divalent linking group

R is a hydrogen, lower alkyl, aryl or alkoxy

Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization

- 5 n is 0 or 1
- m is an integer from 1 to 3
- wherein C comprises from 0.01% to 50% of the copolymer; and
- (b) from 0.5% to 99.5% of a carrier suitable for application to hair.
- 10 2. A hair care composition according to Claim 1 characterized in that the copolymer comprises from 5% to 98% A monomer, from 0.01% to 50% C monomer and from 0% to 98% B monomer.
- 3. A hair care composition according to Claim 1 characterized in that the copolymer comprises from 0% to 98% A monomer, from 0.01% to 50% C monomer, and from 7.5% to 80% B monomer.
- 4. A hair care composition characterized in that it comprises:
- 15 (a) from 0.1% to 10.0% of a silicone-containing copolymer containing a silicone portion having a molecular weight of from 1,000 to 50,000 which is covalently attached to a non-silicone portion; and
- (b) from 0.5% to 99.5% of a carrier suitable for application to hair;
- the copolymer and carrier selected such that, when dried, the copolymer phase separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion.
- 20 5. A hair care composition characterized in that it comprises:
- (a) from 0.1% to 10.0% of a silicone-containing copolymer having a vinyl polymeric backbone and having grafted to the backbone a polydimethylsiloxane macromer having a weight average molecular weight between 1,000 and 50,000; and
- (b) from 0.5% to 99.5% of a carrier suitable for application to hair;
- the polymer and carrier selected such that, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone.
- 25 6. A hair care composition according to any of Claims 1-5 characterized in that it is in the form of a shampoo which additionally comprises from 10% to 30% of a synthetic surfactant, preferably selected from alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.
- 7. A hair care composition according to any of Claims 1-5 characterized in that it is in the form of a conditioner in which the carrier comprises from 0.1% to 10.0% of a lipid vehicle material, preferably selected from cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof;
- 30 8. A hair care composition according to any of Claims 1-5 characterized in that it is in a form selected from hair sprays, mousses, hair tonics, and gels.
- 9. A method of conditioning and styling hair characterized in that it comprises applying to the hair an effective amount of the composition according to any of Claims 1-8.
- 40 10. A copolymer, having a molecular weight of from 10,000 to 1,000,000, which has a vinyl polymeric backbone having grafted to it monovalent siloxane polymeric moieties, said copolymer comprising from 0.01% to 50% C monomers, from 5% to 98% A monomers, and from 0% to 98% B monomers, wherein:
- A is selected from t-butyl acrylate, t-butyl methacrylate, and mixtures thereof;
- B is at least one reinforcing monomer copolymerizable with A selected from polar monomers and
- 45 macromers, and is preferably selected from acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof; and
- C is a polymeric monomer having a molecular weight of from 1,000 to 50,000 and the general formula
- X(Y)_nSi(R)_{3-m}(Z)_m wherein
- X is a vinyl group copolymerizable with the A and B monomers
- 50 Y is a divalent linking group
- R is a hydrogen, lower alkyl, aryl or alkoxy
- Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from said vinyl polymeric backbone after polymerization
- 55 n is 0 or 1, and
- m is an integer from 1 to 3.
- 11. Copolymers according to Claim 10 characterized in that they are selected from t-butylacrylate/t-butylmethacrylate/(PDMS macromer - 10,000 molecular wt) 56/24/20

t-butylacrylate/(PDMS macromer ~ 10,000 molecular wt.) 80/20
t-butylacrylate/acrylic acid/(PDMS macromer-10,000 molecular wt.) 75/5/20, and mixtures thereof; which are
preferably dissolved in a cyclomethicone solvent.'

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(54) Hair conditioning and styling compositions.

(57) Hair care compositions which provide improved styling and hair conditioning properties are disclosed. These compositions comprise from about 0.1% to about 10.0% of a specifically-defined silicone copolymer and from about 0.5% to about 99.5% of a carrier suitable for application to hair.

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HAIR CONDITIONING AND STYLING COMPOSITIONS

TECHNICAL FIELD

This application is a continuation-in-part of U.S. Application Serial No. 390,559, Torgerson, Bolich and 5 Garbe, filed August 7, 1989.

The present invention relates to hair care compositions which have improved hair conditioning and style retention properties while still leaving the hair with a natural non-sticky feel. These compositions utilize a group of specific silicone macromer-containing copolymers.

10

BACKGROUND OF THE INVENTION

The desire to have hair retain a particular shape is widely held. Such style retention is generally 15 accomplished by either of two routes: permanent chemical alteration or temporary alteration of hair style/shape. A temporary alteration is one which can be removed by water or by shampooing. Temporary style alteration has generally been accomplished by means of the application of a composition to dampened hair after shampooing and/or conditioning and prior to drying and/or styling. The materials used to provide setting benefits have generally been resins or gums and have been applied in the form of 20 mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following shampooing/conditioning to apply the styling composition. In addition, since the style hold is provided by resin materials which set-up on the hair, the hair tends to feel sticky or stiff after application and it is difficult to restyle the hair without further application of the styling composition.

25 It has now been discovered that hair care compositions comprising certain specifically-defined silicone macromer-containing copolymers provide excellent hair style retention benefits, together with hair conditioning. The compositions may be in any of the conventional forms including, but not limited to, shampoos, conditioners, hair sprays, tonics, lotions, gels, and mousses. The compositions provide these benefits to hair without leaving the hair with a stiff or sticky/tacky feel and without negatively affecting dry hair 30 properties, such as ease of combing. Further, hair to which the compositions of the present invention have been applied may be restyled several times without requiring reapplication of the compositions.

These results are surprising since other materials which have been typically used in hair care compositions to provide style retention, such as resins and gums, generally hurt dry hair properties (e.g., combing) and leave hair with a sticky and/or stiff feel. Furthermore, silicone materials typically used for hair 35 conditioning tend to hurt style retention.

Siloxanes (see, for example, U.S. Patent 3,208,911, Oppliger, issued September 28, 1965) and siloxane-containing polymers have been taught for use in hair conditioning compositions. U.S. Patent 4,601,902, Fridd et al., issued July 22, 1986, describes hair conditioning or shampoo/conditioner compositions which include a polydiorganosiloxane having quaternary ammonium substituted groups attached to the silicon, and 40 a polydiorganosiloxane having silicon-bonded substituents which are amino-substituted hydrocarbon groups. U.S. Patent 4,654,161, Kollmeier et al., issued March 31, 1987, describes a group of organopolysiloxanes containing betaine substituents. When used in hair care compositions, these compounds are said to provide good conditioning, compatibility with anionic components, hair substantivity, and low skin irritation. U.S. Patent 4,563,347, Starch, issued January 7, 1986, relates to hair conditioning compositions which include 45 siloxane components containing substituents to provide attachment to hair. Japanese Published Application 56-129,300, Lion Corporation, published October 9, 1981, relates to shampoo conditioner compositions which include an organopolysiloxane-oxyalkylene copolymer together with an acrylic resin. U.S. Patent 4,479,893, Hirota et al., issued October 30, 1984, describes shampoo conditioner compositions containing a phosphate ester surfactant and a silicon derivative (e.g., polyether- or alcohol-modified siloxanes). 50 Polyether-modified polysiloxanes are also disclosed for use in shampoos in U.S. Patent 3,957,970, Korkis, issued May 18, 1976. U.S. Patent 4,185,087, Morlino, issued January 22, 1980, describes quaternary nitrogen derivatives of trialkylamino hydroxy organosilicon compounds which are said to have superior hair conditioning properties.

Siloxane-derived materials have also been used in hair styling compositions. Japanese Published Application 56-092,811, Lion Corporation, published December 27, 1979, describes hair setting composi-

tions which comprise an amphoteric acrylic resin, a polyoxyalkylene-denatured organopolysiloxane, and polyethylene glycol. U.S. Patent 4,744,978, Homan et al., issued May 17, 1988, describes hair styling compositions (such as hair sprays) which include the combination of a carboxyfunctional polydimethylsiloxane and a cationic organic polymer containing amine or ammonium groups. Hair styling compositions which 5 include polydiorganosiloxanes and a cationic organic polymer are taught in U.S. Patent 4,733,677, Gee et al., issued March 29, 1988, and U.S. Patent 4,724,851, Cornwall et al., issued February 16, 1988. Finally, European Patent Application 117,360, Cantrell et al., published September 5, 1984, discloses compositions, containing a siloxane polymer having at least one nitrogen-hydrogen bond, a surfactant, and a solubilized titanate, zirconate or germanate, which act as both a conditioner and a hair styling aid.

10 Siloxane-containing polymers have also been used in non-hair care applications. U.S. Patent 4,136,250, Mueller et al., issued January 23, 1979, relates to polymeric materials used in biological contexts where oxygen permeable and tissue compatible membranes are required. They can also be used as carriers for biologically-active substances. These materials are hydrophilic water-insoluble gels which include a low molecular weight terminal olefinic siloxane macromer and a polymer containing water-soluble monoolefinic 15 monomer. U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, describes pressure sensitive adhesive compositions which include a copolymer with a vinyl polymeric backbone having grafted thereto polysiloxane moieties. U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, relates to adhesive release coating compositions which comprise polysiloxane-grafted copolymers and blends of those copolymers with other polymeric materials. None of these last three patents suggest the use of the 20 disclosed siloxane-containing polymers in hair care compositions.

It is an object of the present invention to formulate hair care compositions which provide effective hair conditioning and style retention properties.

It is also an object of the present invention to formulate hair care compositions which provide conditioning and style retention from a single composition.

25 It is a further object of the present invention to formulate hair care compositions which provide good style retention without leaving hair with a stiff or sticky/tacky feel.

It is a further object of the present invention to provide an improved method for styling and conditioning hair.

These and other objects will become readily apparent from the detailed description which follows.

30 Unless otherwise indicated, all percentages and ratios herein are by weight.

SUMMARY OF THE INVENTION

35 The present invention relates to hair care compositions comprising

(a) from about 0.1% to about 10.0% of a silicone-containing copolymer having a vinyl polymeric backbone, preferably having a Tg above about -20°C, and having grafted to the backbone a polydimethylsiloxane macromer having a weight average molecular weight between about 1,000 and about 40 50,000; and

(b) from about 0.5% to about 99.5% of a carrier suitable for application to hair;

the polymer and carrier are selected such that, when dried, the polymer phase-separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which 45 includes the backbone. Preferred silicone-containing copolymers are those having a molecular weight of from about 10,000 to about 1,000,000 and comprising C monomers and components selected from A monomers, B monomers, and mixtures thereof, wherein A is a lipophilic, low polarity free radically polymerizable vinyl monomer, such as methacrylic or acrylic esters; B comprises a hydrophilic polar monomer which is copolymerizable with A, such as acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, vinyl pyrrolidone, or quaternized dimethylaminoethylmethacrylate; and 50 C is a silicone-containing macromer having a weight average molecular weight of from about 1,000 to about 50,000, based on polydimethylsiloxane. These polymers contain from about 0.1% to about 50.0% of C macromer and from about 50.0% to about 99.9% of the combination of A and B monomers.

DETAILED DESCRIPTION OF THE INVENTION

The essential, as well as the optional, components of the present invention are described below.

Silicone-Containing Copolymer

The compositions of the present invention contain from about 0.1% to about 10.0%, preferably from about 0.5% to about 8.0%, of specifically-defined silicone-containing copolymers. It is these polymers which provide the unique hair conditioning and hair setting characteristics of the present invention. The polymers should have a weight average molecular weight of from about 10,000 to about 1,000,000 (preferably from about 30,000 to about 300,000) and, preferably, have a Tg of at least about -20°C. As used herein, the abbreviation "Tg" refers to the glass transition temperature of the non-silicone backbone; and the abbreviation "Tm" refers to the crystalline melting point of the non-silicone backbone, if such a transition exists for a given polymer.

In its broadest sense, the polymers useful in the hair care compositions of the present invention include all properly defined copolymers of silicone with a non-silicone adhesive polymer. To be useful such copolymers should satisfy the following four criteria:

- 15 (1) when dried the copolymer phase-separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the non-silicone portion;
- (2) the silicone portion is covalently attached to the non-silicone portion;
- (3) the molecular weight of the silicone portion is from about 1,000 to about 50,000; and
- 20 (4) the non-silicone portion must render the entire copolymer soluble or dispersible in the hair care composition vehicle and permit the copolymer to deposit on hair. In addition to the graft copolymers described above, useful copolymers include block copolymers containing up to about 50% (preferably from about 10% to about 20%) by weight of one or more polydimethyl siloxane blocks and one or more non-silicone blocks (preferably acrylates or vinyls).

Preferred polymers comprise a vinyl polymeric backbone, preferably having a Tg above about -20°C and, grafted to the backbone, a polydimethylsiloxane macromer having a weight average molecular weight of from about 1,000 to about 50,000, preferably from about 5,000 to about 40,000, most preferably about 20,000. The polymer is such that when it is formulated into the finished hair care composition, when dried, the polymer phase separates into a discontinuous phase which includes the polydimethylsiloxane macromer and a continuous phase which includes the backbone. It is believed that this phase separation property provides a specific orientation of the polymer on hair which results in the desired hair conditioning and setting benefits. The phase-separating nature of the compositions of the present invention may be determined as follows:

The polymer is cast as a solid film out of a good solvent (i.e., a solvent which dissolves both the backbone and the silicone). This film is then sectioned and examined by transmission electron micrography. Microphase separation is demonstrated by the observation of inclusions in the continuous phase. These inclusions should have the proper size to match the size of the silicone chain (typically a few hundred nm or less) and the proper density to match the amount of silicone present. This behavior is well documented in the literature for polymers with this structure (see, for example, S. D. Smith, Ph.D. Thesis, University of Virginia, 1987, and references cited therein).

A second method for determining phase-separating characteristics involves examining the enrichment of the concentration of silicone at the surface of a polymer film relative to the concentration in the bulk polymer. Since the silicone prefers the low energy air interface, it preferentially orients on the polymer surface. This produces a surface which is entirely covered by silicone even when the concentration of the silicone by weight in the whole polymer is low (2% to 20%). This is demonstrated experimentally by ESCA (electron spectroscopy for chemical analysis) of the dried film surface. Such an analysis shows a high level of silicone and a greatly reduced level of backbone polymer when the film surface is analyzed. (Surface here means the first few tens of Angstroms of film thickness.) By varying the angle of the interrogating beam the surface can be analyzed to varying depths.

In its broadest aspect, the copolymers utilized in the present application comprise C monomers together with monomers selected from the group consisting of A monomers, B monomers, and mixtures thereof. These copolymers contain at least A or B monomers, together with C monomers, and preferred copolymers contain A, B and C monomers.

Examples of useful copolymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, and U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference. These copolymers are comprised of monomers A, C and, optionally, B, which are defined as follows. A is at least one free radically polymerizable vinyl monomer or monomers. B, when used, comprises at least one reinforcing monomer copolymerizable with A and is selected from the group consisting of polar monomers and macromers

having a T_g or a T_m above about -20 °C. When used, B may be up to about 98%, preferably up to about 80%, more preferably up to about 20%, of the total monomers in the copolymer. Monomer C comprises from about 0.01% to about 50.0% and the total monomers in the copolymer.

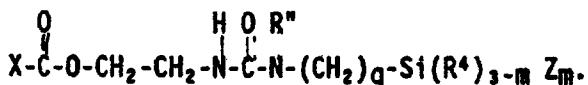
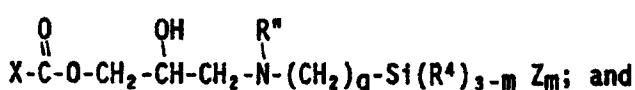
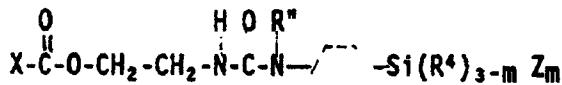
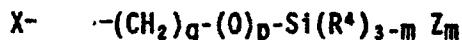
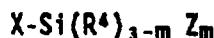
Representative examples of A (hydrophobic) monomers are the acrylic or methacrylic acid esters of C₁-

5 C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, 10 and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred A monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

15 Representative examples of B (hydrophilic) monomers include acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butylacrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (produced by the hydrolysis of vinyl acetate after polymerization) vinyl caprolactam, and mixtures thereof. Preferred B monomers include acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof.

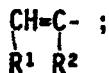
The C monomer has the general formula

25 wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a
hydrogen, lower alkyl, aryl or alkoxy; Z is a monovalent siloxane polymeric moiety having a number
average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions
and is pendant from the vinyl polymeric backbone, described above; n is 0 or 1; and m is an Integer from 1
30 to 3. C has a weight average molecular weight of from about 1,000 to about 50,000, preferably from about
5,000 to about 40,000, most preferably from about 10,000 to about 20,000. Preferably, the C monomer has
a formula selected from the following group:



In those structures, m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; R" is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; X is

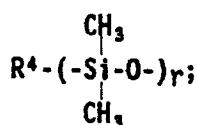
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R¹ is hydrogen or -COOH (preferably R¹ is hydrogen); R² is hydrogen, methyl or -CH₂COOH (preferably R² is methyl); Z is

15



R⁴ is alkyl, alkoxy, alkylamino, aryl, or hydroxyl (preferably R⁴ is alkyl); and r is an integer from about 5 to about 700 (preferably r is about 250).

20

The polymers of the present invention generally comprise from 0% to about 98% (preferably from about 5% to about 98%, more preferably from about 50% to about 90%) of monomer A, from about 0% to about 98% (preferably from about 7.5% to about 80%) of monomer B, and from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of monomer C. The combination of the A and B monomers preferably comprises from about 50.0% to about 99.9% (more preferably about 60% to about 99%, most preferably from about 75% to about 95%) of the polymer. The composition of any particular copolymer will help determine its formulation properties. In fact, by appropriate selection and combination of particular A, B and C components, the copolymer can be optimized for inclusion in specific vehicles. For example, polymers which are soluble in an aqueous formulation preferably have the composition: from about 0% to about 70% (preferably from about 5% to about 70% monomer A, from about 30% to about 98% (preferably from about 30% to about 80% monomer B, and from about 1% to about 40% monomer C. Polymers which are dispersible have the preferred composition: from about 0% to about 70% (more preferably from about 5% to about 70%) monomer A, from about 20% to about 80% (more preferably from about 20% to about 60%) monomer B, and from about 1% to about 40% monomer C.

25

In one aspect of the present invention, the polymers comprise from about 5% to about 98% A monomer, from about 0.01% to about 50% C monomer, and from 0% to about 98% B monomer. In these polymers, it is preferred that A be selected from t-butylacrylate, t-butylmethacrylate, and mixtures thereof, since such polymers can be dissolved directly in cyclomethicone solvents without requiring co-solvents. This is surprising in view of U.S. Patents 4,693,935 (Mazurek) and 4,728,571 (Clemens et al.) which suggest that tertiary alcohols are not suitable A monomers.

30

Particularly preferred polymers for use in the present invention include the following (the weight percents below refer to the amount of reactants added in the polymerization reaction, not necessarily the amount in the finished polymer):

acrylic acid/n-butylmethacrylate/(polydimethylsiloxane (PDMS) macromer-20,000 molecular weight) (10/70/20 w/w/w) (I)

35

N,N-dimethylacrylamide/isobutyl methacrylate/(PDMS macromer -20,000 molecular weight) (20/60/20 w/w/w) (II)

dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexylmethacrylate/(PDMS macromer-20,000 molecular weight) (25/40/15/20 w/w/w/w) (III)

dimethylacrylamide/(PDMS macromer - 20,000 molecular weight) (80/20 w/w) (IV)

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t-butylacrylate/t-butylmethacrylate/(PDMS macromer - 10,000 molecular weight) (56/24/20 w/w/w) (V)

t-butylacrylate/(PDMS macromer - 10,000 molecular weight) (80/20 w/w) (VI)

t-butylacrylate/N,N-dimethylacrylamide/(PDMS macromer -10, 000 molecular weight) (70/10/20) (VII)

t-butylacrylate/acrylic acid/(PDMS macromer - 10,000 molecular weight) (75/5/20) (VIII)

45

The silicone-containing copolymers described above are synthesized as follows.

50

The polymers are synthesized by free radical polymerization methods, the general principles of which are well understood. See, for example, Odian, "Principles of Polymerization", 2nd edition, John Wiley & Sons, 1981, pp. 179-318. (isher, date, pages). The desired monomers are all placed in a reactor, along with a sufficient amount of a mutual solvent so that when the reaction is complete the viscosity of the reaction is

reasonable. Typical monomer loadings are from about 20% to about 50%. Undesired terminators, especially oxygen, are removed as needed. This is done by evacuation or by purging with an inert gas, such as argon or nitrogen. The initiator is introduced and the reaction brought to the temperature needed for initiation to occur, assuming thermal initiators are used. Alternatively, redox or radiation initiation can be used as desired.

5 The polymerization is allowed to proceed as long as needed for a high level of conversion to be achieved, typically from a few hours to a few days. The solvent is then removed, usually by evaporation or by precipitating the polymer by addition of a nonsolvent. The polymer is further purified as needed.

By way of example, Polymers I, II and III, described above, are synthesized in the following manner. There are numerous variations on these procedures which are entirely up to the discretion of the synthetic chemist (e.g., choice of degassing method and gas, choice of initiator type, extent of conversion, reaction loading, etc). The choice of initiator and solvent are often determined by the requirements of the particular monomers used, since different monomers have different solubilities and different reactivities to a specific initiator.

10 Polymer I: Place 10 parts acrylic acid, 70 parts n-butylmethacrylate, and 20 parts 20K PDMS macromer in a flask. Add sufficient ethyl acetate to produce a final monomer concentration of 40%. Add initiator, benzoyl peroxide, to a level of 0.5% by weight relative to the amount of monomer. Evacuate the vessel, and refill with nitrogen. Heat to 60 °C and maintain this temperature for 48 hours while agitating. Terminate the reaction by cooling to room temperature, and dry off the ethyl acetate by pouring the reaction mixture into a teflon-coated pan and placing in a vacuum oven.

15 Polymer II: Place 20 parts N,N-dimethylacrylamide, 60 parts isobutylmethacrylate, and 20 parts silicone macromer in a reaction vessel fitted with a temperature probe, reflux condenser, inlet port, and argon sparge. Add sufficient toluene to bring the final monomer concentration to 20% by weight. Sparge with argon for 1 to 2 hours. While sparging, heat to 62 °C, with a sufficient rate of argon flow to keep the solution mixed. Add initiator, azobisisobutyronitrile, to a level of 0.25% by weight relative to the weight of monomer present. Monitor the reaction visually, ensuring that no phase separation of reactants occurs during polymerization. If any turbidity is observed, add sufficient warm degassed toluene to eliminate the turbidity. Continue to monitor throughout the reaction. Terminate the reaction after 4 to 6 hours and purify as with Polymer I.

20 Polymer III: Place 25 parts dimethylaminoethylmethacrylate, 15 parts 2-ethylhexylmethacrylate, 40 parts isobutylmethacrylate, and 20 parts 20K PDMS macromer in a reaction vessel fitted with a mechanical stirrer, argon sparge, temperature probe, reflux condenser and inlet port. Add sufficient toluene to bring the final monomer concentration to 30% by weight. Begin stirring and sparge with argon for 2 hours. While sparging, heat to 60 °C in a water bath. Add initiator, azobisisobutyronitrile, to a level of 0.15% by weight relative to the weight of monomer present. Continue stirring and a slow argon sparge and maintain the reaction temperature at 60 °C. Allow to react for 24 hours. Terminate the reaction and remove the solvent as with Polymer I.

Carrier

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The compositions of the invention also comprise a carrier, or a mixture of such carriers, which are suitable for application to hair. The carriers are present at from about 0.5% to about 99.5%, preferably from about 5.0% to about 99.5%, most preferably from about 10.0% to about 90.0%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate carrier will also depend on the particular copolymer to be used, and whether the product formulated is meant to be left on hair (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

45 The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions. The solvent selected must be able to dissolve or disperse the particular silicone copolymer being used. The nature and proportion of B monomer in the copolymer largely determines its polarity and solubility characteristics. The silicone copolymers can be designed, by appropriate combination of monomers, for formulation with a wide range of solvents. Suitable solvents for use in the present invention include, but are not limited to, water, lower alcohols (such as ethanol, isopropanol), hydro-alcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane,

octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane), and mixtures thereof. Preferred solvents include water, ethanol, volatile silicon derivatives, and mixtures thereof. The solvents used in such mixtures may be miscible or immiscible with each other.

Where the hair care compositions are conditioner compositions, the carrier may include gel vehicle materials. This gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail below. Gel-type vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkytrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972).

The vehicles may incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is present at from about 0.5% to about 5.0% of the composition.

Preferred esters for use herein include cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Preferred vehicles for use in the compositions of the present invention include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA). These vehicles are described in detail in the following three concurrently-filed patent applications: Vehicle System for Use in Hair Care Compositions, Bolich, Norton and Russell, Docket numbers 4000, 4001, and 4002, incorporated herein by reference.

Other carriers, suitable for use with the present invention are, for example, those used in the formulation of tonics, mousse, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousse and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also require an emulsifying agent to keep the silicone copolymer homogeneously dispersed in solution. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. If such an emulsifying agent is used, it is present at a level of from about 0.25% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

50

Optional Ingredients

The hair care compositions of the present invention may be formulated in a wide variety of product types, including mousse, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components required to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. The following is a description of some of these additional components.

Surfactants

Surfactants are preferred optional ingredients in the compositions of the invention, particularly shampoo and conditioner compositions. When present, the surfactant comprises from about 0.05% to about 50% of the composition. For a shampoo, the level is preferably from about 10% to about 30%, most preferably from about 12% to about 25%, of the composition. For conditioners, the preferred level of surfactant is from about 0.2% to about 3%. Surfactants useful in compositions of the present invention include anionic, nonionic, cationic, zwitterionic and amphoteric surfactants.

Synthetic anionic detergents useful herein, particularly for shampoo compositions, include alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. The alkyl ether sulfates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from about 10 to about 20 carbon atoms. Preferably, R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred herein. Such alcohols are reacted with about 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which may be used in the present invention are sodium coconut alkyl triethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from about 0 to about 20% by weight C_{12-13} compounds; from about 60 to about 100% by weight of $\text{C}_{14-15-16}$ compounds, from about 0 to about 20% by weight of $\text{C}_{17-18-19}$ compounds; from about 3 to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45 to about 90% by weight of compounds having a degree of ethoxylation of from about 1 to about 4; from about 10 to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1 to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein R_1 is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, ineso-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{12-18} n-paraffins.

Additional examples of anionic synthetic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfosuccinamate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diethyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α -olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , etc., when used in the

gaseous form.

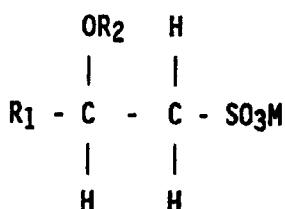
The α -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

10 A specific α -olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, Pflaumer and Kessler, issued July 25, 1967, incorporated herein by reference.

Another class of anionic organic surfactants are the β -alkyloxy alkane sulfonates. These compounds have the following formula:

15



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where R_1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R_2 is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

25 Specific examples of β -alkyloxy-alkane-1-sulfonates, or alternatively 2-alkyloxy-alkane-1-sulfonates, having low hardness (calcium ion) sensitivity useful herein include: potassium- β -methoxydecanesulfonate, sodium 2-methoxy-tridecanesulfonate, potassium 2-ethoxytetradecylsulfonate, sodium 2-isopropoxyhexadecylsulfonate, lithium 2-t-butoxytetradecylsulfonate, sodium β -methyoxyoctadecylsulfonate, and ammonium β -n-propoxydodecylsulfonate.

30 Many additional nonsoap synthetic anionic surfactants are described in McCutcheon's. Detergents and Emulsifiers 1984 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference. Also U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, discloses many other anionic as well as other surfactant types and is incorporated herein by reference.

35 Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitterionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

40 1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

45 2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of about 2,500 to about 3,000, are satisfactory.

50 3. The condensation product of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 10 to about 14 carbon atoms.

55 4. Long chain tertiary amine oxides corresponding to the following general formula:



wherein R₁ contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glycetyl moiety, and R₂ and R₃ contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyl-dodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyl-decylamine oxide, dimethyl-tetradecylamine oxide, 3,6,9-trioxaheptadecyl diethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl dimethylamine oxide, 3-dodecoxy-2-hydroxypropyl(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glycetyl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylmethylethylphosphine oxide, 3,6,9-trioxaoctadecylmethylphosphine oxide, cetyltrimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyl(2-hydroxyethyl) phosphine oxide, stearyldimethylphosphine oxide, cetylethylpropylphosphine oxide, oleyldiethylphosphine oxide, dodecyldiethylphosphine oxide, tetradecyl diethylphosphine oxide, dodecyldipropylphosphine oxide, dodecyldi(hydroxymethyl)phosphine oxide, dodecyldi(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxypropylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydodecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glycetyl moiety. Examples include: octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, Issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983. If included in the compositions of the present invention, the cationic surfactant is present at from about 0.05% to about 5%.

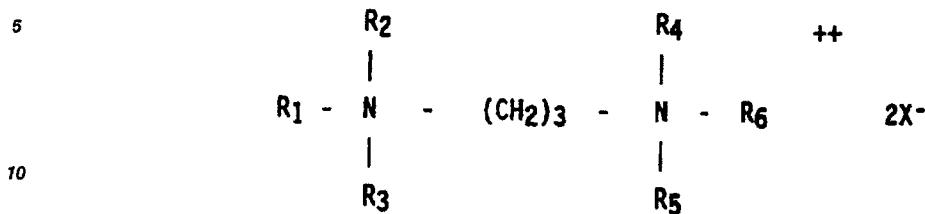
Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



55 wherein R₁- R₄ are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and X is an anion selected from halogen, acetate, phosphate, nitrate and

alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups.

Other quaternary ammonium salts useful herein have the formula:

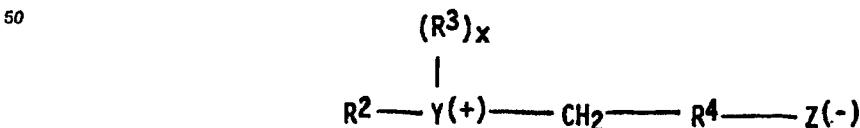


wherein R₁ is an aliphatic group having from about 16 to about 22 carbon atoms, R₂, R₃, R₄, R₅, and R₆ are selected from hydrogen and alkyl having from about 1 to about 4 carbon atoms, and X is an ion selected from halogen, acetate, phosphate, nitrate and alkyl sulfate radicals. Such quaternary ammonium salts include tallow propane diammonium dichloride.

Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R₁ and R₂ have predominately from 16 to 18 carbon atoms). Examples of quaternary ammonium salts useful in the present invention include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl) dimethyl ammonium chloride, and stearyl dimethyl benzyl ammonium chloride. Ditallow dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and cetyl trimethyl ammonium chloride are preferred quaternary ammonium salts useful herein. Di-(hydrogenated tallow) dimethyl ammonium chloride is a particularly preferred quaternary ammonium salt.

Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidyl behenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride and stearamidopropyl dimethylamine citrate. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Patent 4,275,055, Nachtingal, et al., issued June 23, 1981, incorporated by reference herein.

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R² contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R³ is an alkyl or monohydroxyalkyl group

containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R⁴ is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

5 Examples of such surfactants include:

- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-5-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecoxylphosphonio]-2-hydroxy-propane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 10 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(i-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 15 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, 20 oleyl dimethyl gammacarboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alphacarboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the RCONH(CH₂)₃ radical is attached to the nitrogen atom of the betaine are also useful in this invention.

25 Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are 30 sodium 3-dodecylaminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

The above-mentioned surfactants can be used alone or in combination in the hair care compositions of 35 the present invention. The alkyl sulfates, ethoxylated alkyl sulfates and mixtures thereof are preferred for use herein.

The hair care compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, 40 e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonooethanol amide, dimethicone copolyols, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as 45 cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, and sodium carbonate; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such 50 as glycerin and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the composition.

The pH of the present compositions should be between about 3 and about 9, preferably between about 4 and about 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

55 The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Methods of making various types of hair care compositions are described more specifically in the following examples.

Method of Use

The hair care compositions of the present invention are used in conventional ways to provide the hair conditioning/styling/hold benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair, which may then be rinsed from the hair (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, and tonic products). By "effective amount" is meant an amount sufficient to provide the hair conditioning/styling/hold benefits desired considering the length and texture of the hair, and the type of product used. Preferably, the product is applied to wet or damp hair prior to drying and styling of the hair. After the compositions of the present invention are applied to the hair, the hair is dried and styled in the usual ways of the user.

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

The following table defines the silicone copolymers used in the examples (weight ratios given refer to proportion added to reaction mix):

Copolymer #1 10/70/20 acrylic acid/n-butylmethacrylate/silicone macromer S2, polymer molecular weight about 100,000
Copolymer #2 10/70/20 dimethylaminoethyl methacrylate/isobutyl methacrylate/silicone macromer S2, polymer molecular weight about 400,000
Copolymer #3 60/20/20 quaternized dimethylaminoethyl methacrylate/isobutyl methacrylate/silicone macromer S1, polymer molecular weight about 500,000
Copolymer #4 40/40/20 acrylic acid/methyl methacrylate/silicone macromer S1, polymer molecular weight about 400,000
Copolymer #5 10/70/20 acrylic acid/n-butyl methacrylate/silicone macromer S1, polymer molecular weight about 300,000
Copolymer #6 25/65/10 acrylic acid/isopropyl methacrylate/silicone macromer S2, polymer molecular weight about 200,000
Copolymer #7 60/25/15 N,N-dimethylacrylamide/methoxyethyl methacrylate/silicone macromer S1, polymer molecular weight about 200,000
Copolymer #8 12/64/4/20 N,N-dimethylacrylamide/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
Copolymer #9 30/40/10/20 dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer S1, polymer molecular weight about 300,000
Copolymer #10 80/20 t-butylacrylate/PDMS macromer S2, polymer molecular weight about 150,000

Silicone macromer S1- has a molecular weight of about 20,000 and is prepared in a manner similar to Example C-2c of U.S. Patent 4,728,571, Clemens, issued March 1, 1988.

Silicone macromer S2- has a molecular weight of about 10,000 and is prepared in a manner similar to Example C-2b of U.S. Patent 4,728,571, Clemens, issued March 1, 1988.

45

EXAMPLE 1

The following is a hair spray composition representative of the present invention

50

Component	Weight %
Silicone Copolymer #4	2.00
Ethanol	72.90
Perfume	0.10
Isobutane propellant	25.00

55

This product is prepared by adding the silicone copolymer and perfume to the ethanol and mixing for

several hours until all the polymer is dissolved. This "concentrate" is then placed in aerosol cans which are fitted with valves crimped under vacuum and then filled through the valve stem with isobutane dispensed by a pressure filler.

5

EXAMPLE II

10

The following is a shampoo composition representative of the present invention.

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Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #2	1.00
Chloropropyl heptamethyl cyclotetrasiloxane	3.00
<u>Premix</u>	
Silicone gum	0.50
Dimethicone, 350 cs. fluid	0.50
<u>Main Mix</u>	
Ammonium lauryl sulfate	11.00
Cocamide MEA	2.00
Ethylene glycol distearate	1.00
Xanthan gum	1.20
Kathon CG ¹	0.04
Citric acid to pH 4.5	q.s.
Double reverse osmosis (DRO) H ₂ O	q.s.

¹ preservative commercially available from Rohm & Haas

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The Styling Agent and Premix are blended separately in a conventional manner. The Main Mix is prepared by first dissolving the xanthan gum in the water with conventional mixing. The remaining Main Mix ingredients are added and the Main Mix is heated to 150° F with agitation for 1/2 hour. The Styling Agent and Premix are then added sequentially with about ten minutes agitation between additions, and the entire mixture is stirred while the batch is cooled to room temperature. For varied particle size, the Styling Agent and Premix can be added at different times using either or both high shear mixing (high speed dispersator) or normal agitation.

EXAMPLE III

45

The following is a shampoo composition representative of the present invention.

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Component	Weight %
Ammonium lauryl sulfate	7.00
Ammonium laureth sulfate	7.00
Cocamide MEA	2.50
Silicone Copolymer #3	1.00
Natrosol 250H ¹	1.00
Glydant ²	0.37
DRO H ₂ O	q.s.

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10

¹ hydroxyethyl cellulose commercially available from Aqualon Co.² preservative commercially available from Glyco, Inc.

15 The shampoo is made by first dispersing the Matrosol and silicone copolymer in the water for about 1 hour with conventional agitation. The remaining ingredients are then added.

EXAMPLE IV

20

The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent Premix</u>	
Silicone Copolymer #8	2.00
Phenethylpentamethyl disiloxane	6.00
Octamethyl cyclotetrasiloxane	3.00
<u>Xanthan Premix</u>	
Xanthan gum	0.25
DRO H ₂ O	25.00
<u>Main Mix</u>	
Dihydrogenated tallow-dimethylammonium chloride (DTDMAC)	0.50
EDTA, disodium salt	0.10
D.C. 929 ¹	2.00
Perfume	0.10
Poly Surf C ²	0.75
Locust bean gum	0.75
Kathon CG ³	0.04
DRO H ₂ O	q.s.

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¹ amodimethicone, commercially available from Dow Corning² hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.³ preservative commercially available from Rohm and Haas

60

55 The Styling Agent and Xanthan Premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating with agitation to 95°C for about 1/2 hour. As the batch is cooled, the Styling Agent and Xanthan Premixes are added at about 60°C with vigorous mixing. The batch is then cooled to ambient temperature.

EXAMPLE V

The following is a styling rinse composition representative of the present invention.

5	<u>Component</u>	<u>Weight %</u>
	<u>Premix A</u>	
	Silicone Copolymer #3	2.00
	DRO H ₂ O	10.00
	<u>Premix B</u>	
10	Silicone Copolymer #4	2.00
	DRO H ₂ O	15.00
	NaOH solution (50%)	0.20
	<u>Main Mix</u>	
15	Poly Surf C ¹	1.00
	Stearamide DEA	0.50
	Ethanol	10.00
	Perfume	0.20
20	DRO H ₂ O	q.s.

¹ hydrophobically-modified hydroxyethyl cellulose, commercially available from Aqualon Co.

25 Both premixes are blended separately in a conventional manner. The Main Mix is prepared by adding all the ingredients together and heating to about 60 °C with mixing. The premixes are then added to the Main Mix with agitation for about 1/2 hour and the batch is cooled to ambient temperature. Either sodium hydroxide or citric acid, if necessary, is added to adjust composition pH to 6.5.

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EXAMPLE VI

35 The following is a hair grooming tonic composition representative of the present invention.

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40	<u>Component</u>	<u>Weight %</u>
	Silicone Copolymer #9	0.70
	Perfume	0.10
	Ethanol	q.s.

45 The composition is made by mixing the above components together in a conventional manner.

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EXAMPLE VII

50 The following is a shampoo composition representative of the present invention.

55

Component	Weight %
Ammonium laureth sulfate	7.00
Cocamido propyl betaine	6.00
Silicone Copolymer #6	2.00
Ethanol	10.00
PEG 150 distearate	2.00
Glydant ¹	0.38
Perfume	1.00
DRO H ₂ O	q.s.

¹ preservative commercially available from Glyco, Inc.

15 The shampoo is prepared by combining the ammonium laureth sulfate (normally supplied as a 28% solution in water) and Silicone Copolymer and heating to 70 °C for about 1/2 hour with mixing. The remaining ingredients are added and mixed for an additional 1/2 hour. The batch is then cooled to ambient temperature. Composition pH is adjusted to 6.5 by the addition of citric acid or sodium hydroxide, if necessary.

20

EXAMPLE VIII

25 The following is a styling rinse composition representative of the present invention.

Component	Weight %
<u>Styling Agent</u>	
Silicone Copolymer #5	3.00
Phenylpentamethyl disiloxane	9.00
<u>Premix</u>	
Silicone Gum GE SE76 ¹	0.50
Decamethyl cyclopentasiloxane	4.00
<u>Main Mix</u>	
Poly Surf C ²	0.60
Locust bean gum	0.50
EDTA, disodium salt	0.15
DTDMAC	0.65
Glydant ³	0.40
DRO H ₂ O	q.s.

46 ¹ Commercially available from General Electric

² hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

³ preservative commercially available from Glyco, Inc.

50

The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95 °C for 1/2 hour with agitation. As the batch is cooled to about 60 °C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

55

EXAMPLE IX

The following is a styling rinse composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
5	<u>Styling Agent</u>	
	Silicone Copolymer #10 Octamethyl cyclotetrasiloxane	3.00 9.00
10	<u>Premix</u>	
	Silicone Gum GE SE76 ¹ Decamethyl cyclopentosiloxane	0.50 4.00
15	<u>Main Mix</u>	
	Poly Surf C ² Stearamide DEA DTDMAC Kathon CG ³ Imiazole Perfume DRO H ₂ O	1.25 0.40 0.50 0.03 0.15 0.10 q.s.
20		
25		

¹ Commercially available from General Electric

² hydrophobically-modified hydroxyethyl cellulose commercially available from Aqualon Co.

³ preservative commercially available from Rohm & Haas

30 The Styling Agent and Premix are blended separately by conventional means. The Main Mix is prepared by adding all the ingredients and heating to 95 °C for 1/2 hour with agitation. As the batch is cooled to about 60 °C, the Premix and Styling Agent mixes are added to the Main Mix with agitation and the batch is cooled to ambient temperature.

EXAMPLE X

The following is a cold-wave hair perm composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
40	Thioglycolic acid	5.00
	Monoethanolamine	6.00
	Silicone Copolymer #3	1.50
45	PEG 10 monostearate	0.50
	DRO H ₂ O	q.s.

50 The composition is prepared by blending all the ingredients with agitation for about 1/2 hour at 60 °C and then cooling to ambient temperature.

EXAMPLE XI

55 The following is a hair conditioner composition representative of the present invention.

	<u>Component</u>	<u>Weight %</u>
	<u>Styling Agent Premix</u>	
5	Silicone Copolymer #9 Phenyl pentamethyl disiloxane	1.00 4.00
	<u>Silicone Premix</u>	
10	Silicone gum, GE SE76 ¹ Octamethyl cyclotetrasiloxane	0.30 1.70
	<u>Main Mix</u>	
15	Cetyl alcohol Quaternium 18 ² Stearyl alcohol Natrosol 250 MBR ³ Ceteareth-20 Fragrance Dimethicone copolyol Citric acid	1.00 0.85 0.70 0.50 0.35 0.20 0.20 0.13
20	Methylchloroisothiazolinone, methylisothiazolinone Sodium chloride DRO H ₂ O	0.04 0.01 q.s.

¹ Commercially available from General Electric

25 ² Diallyl quaternary ammonium compound, commercially available from Sherex

³ hydroxyethyl cellulose material, commercially available from Aqualon Co.

30 The product is prepared by comixing all the Main Mix ingredients, heating to about 60 °C with mixing, and colloid milling down to about 45 °C. At this temperature, the two premixes are added separately with moderate agitation and the batch allowed to cool to ambient temperature.

35

EXAMPLE XII

The following is a styling gel composition representative of the present invention.

40

	<u>Component</u>	<u>Weight %</u>
	Silicone Copolymer #7	2.00
45	Carbopol 940 ¹	0.75
	Triethanolamine	1.00
	Dye solution	0.05
	Perfume	0.10
	Laureth-23	0.10
50	DRO H ₂ O	q.s.

¹ cross-linked polyacrylic acid, commercially available from B. F. Goodrich

55

This batch is made by mixing the listed components together in a conventional manner.

EXAMPLE XIII

The following is a hair mousse composition representative of the present invention.

	Component	Weight %
5	Silicone Copolymer #7	3.00
	Ethanol	15.00
	Cocamine oxide	0.60
	D.C. 190 ¹	0.20
10	Cocamide DEA	0.30
	Perfume	0.10
	Isobutane	7.00
	DRO H ₂ O	q.s.

¹ dimethicone copolyol, commercially available from Dow Corning

15

The composition is made by blending all of the ingredients except isobutane at ambient temperature until well mixed. Aluminum aerosol cans are then filled with 95 parts of this batch, affixed with a valve which is crimped into position, and lastly pressure filled with 5 parts isobutane.

20

EXAMPLE XIV

25 The following is a pump hair spray composition representative of the present invention.

	Component	weight %
30	Silicone Copolymer #1	2.50
	Dibutyl phthalate	0.20
	Phenylmethicone	0.30
	Perfume	0.05
	Aminomethyl propanol	0.20
35	Ethanol	q.s.

This composition is made by mixing the listed components together in a conventional manner.

When the compositions defined in Examples I-XIV are applied to hair in the conventional manner, they provide effective hair conditioning and styling/hold benefits without leaving the hair with a sticky/stiff feel.

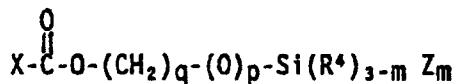
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Claims

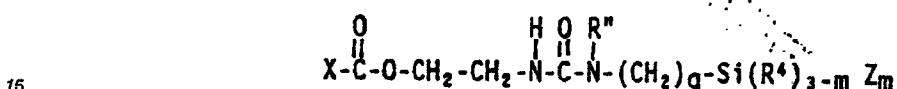
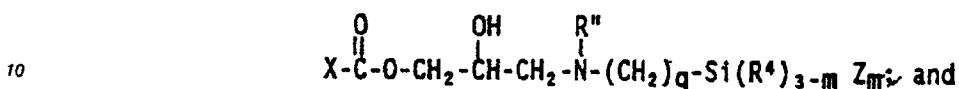
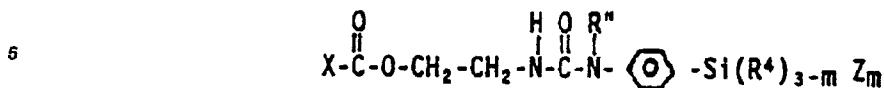
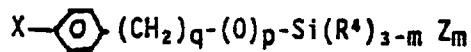
45 1. A hair care composition characterized in that it comprises:
 (a) from 0.1% to 10.0% of a silicone-containing copolymer having a molecular weight of from 10,000 to 1,000,000 comprising a component selected from: a lipophilic low polarity free radically polymerizable vinyl monomer (A), a hydrophilic polar monomer which is copolymerizable with A (B), and mixtures thereof; together with a silicone-containing macromer (C) having a weight average molecular weight of from 1,000 to 50,000 preferably from 5,000 to 40,000, based on polydimethylsiloxane selected from

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X-Si(R⁴)_{3-m}Z_m



wherein m is 1, 2 or 3; p is 0 or 1; R" is alkyl or hydrogen; q is an integer from 2 to 6; s is an integer from 0 to 2; X is



25 R¹ is hydrogen or -COOH; R² is hydrogen, methyl or -CH₂COOH; Z is



R⁴ is alkyl, alkoxy, alkylamino, aryl or hydroxyl; and r is an integer from 5 to 700; and wherein the silicone-containing copolymer comprises from 0% to 98% monomer A, from 0% to 98% monomer B, and from 0.1% to 50% monomer C; and

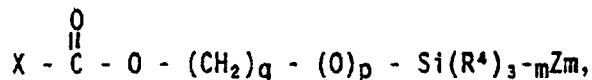
35 (b) from 0.5% to 99.5% of a carrier suitable for application to hair.

2. A hair care composition according to Claim 1 characterized in that the silicone-containing copolymer comprises from 5% to 98% monomer A, from 7.5% to 80% monomer B, and from 0.1% to 50% monomer C.

40 3. A hair care composition according to Claim 1 or 2 characterized in that monomer A is selected from acrylic acid esters of C₁-C₁₈ alcohols, methacrylic acid esters of C₁-C₁₈ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alphamethylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof; and is preferably selected from n-butylmethacrylate, isobutylmethacrylate, 2-ethylhexylmethacrylate, methylmethacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

45 4. A hair care composition according to any of Claims 1-3 characterized in that monomer B is selected from acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride, half esters of maleic anhydride, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl pyrrolidone, vinyl ethers, maleimides, vinyl pyridine, vinyl imidazole, styrene sulfonate, allyl alcohol, vinyl alcohol, vinyl caprolactam, and mixtures thereof; and is preferably selected from acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, vinyl pyrrolidone, and mixtures thereof.

50 5. A hair care composition according to any of Claim 1-4 characterized in that monomer C has the formula



5 preferably wherein p = 0 and q = 3, m is 1, r is about 250, R⁴ is alkyl, R¹ is hydrogen, and R² is methyl.

6. A hair care composition according to any of Claims 1-5 characterized in that the silicone-containing copolymer is selected from:

acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer - 20,000 mw (10/70/20);

N,N-dimethylacrylamide/isobutyl methacrylate/PDMS macromer -20,000 mw (20/60/20);

10 dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl methacrylate/PDMS macromer - 20,000 mw (25/40/15/20);

dimethylaminoethyl methacrylate/isobutyl methacrylate/PDMS macromer - 20,000 mw (10/70/20);

quaternized dimethylaminoethyl methacrylate/isobutyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);

15 acrylic acid/methyl methacrylate/PDMS macromer - 20,000 mw (40/40/20);

acrylic acid/isopropyl methacrylate/PDMS macromer - 20,000 mw (25/65/10);

N,N-dimethylacrylamide/methoxyethyl methacrylate/PDMS macromer -20,000 mw (60/25/15);

dimethylacrylamide/PDMS macromer - 20,000 mw (80/20); and mixtures thereof.

7. A hair care composition according to any of Claims 1-6 characterized in that it is in the form of a shampoo which additionally comprises from 10% to 30% of a synthetic surfactant, which is preferably selected from alkyl sulfates, ethoxylated alkyl sulfates, and mixtures thereof.

20 8. A hair care composition according to any of Claims 1-6 characterized in that it is in the form of a conditioner in which the carrier comprises from 0.1% to 20.0% of a lipid vehicle material, preferably selected from cetyl alcohol, stearyl alcohol, cetyl palmitate, glyceryl monostearate, and mixtures thereof; and from 0.05% to 5.0% of a cationic surfactant, preferably a quaternary ammonium surfactant.

9. A hair care composition according to any of Claims 1-6 characterized in that it is in a form selected from hair sprays, mousses, hair tonics and gels.

10. A method of conditioning and styling hair characterized in that it comprises applying to the hair an effective amount of the composition according to any of Claims 1-9.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 8391

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 834 972 (ALLIED-SIGNAL INC.) * Column 1, line 40 - column 2, line 27 * ---	1-10	A 61 K 7/06 A 61 K 7/48
A	CHEMICAL ABSTRACTS, vol. 88, 1978, page 271, abstract no. 54975g, Columbus, Ohio, US; & JP-A-77 57 337 (MATSUSHITA ELECTRIC WORKS, LTD) 11-05-1977 * Abstract * ---	1-10	
A,D	US-A-4 136 250 (CIBA-GEIGY CO.) * Claims 1-17 *	1-10	
A,D	US-A-4 728 571 (MINNESOTA MINING & MANUFACTURING CO.) * Claims 1-14 *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)			
A 61 K			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	27-11-1990	BERTOCCHI C.	
CATEGORY OF CITED DOCUMENTS			
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(54) Title: HAIR SPRAY COMPOSITIONS WITH IONIC STYLING POLYMER					
(57) Abstract					
<p>Liquid hair styling composition useful for spray application to hair which comprises: (a) an ionic hair styling polymer having a weight average molecular weight of at least about 300,000; (b) a liquid vehicle selected from the group consisting of water, C₁-C₆ monohydric alcohols, and mixtures thereof; (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of non-surface active cations and anions, wherein said cations and anions are at least partially soluble in said liquid carrier; said composition having a pH of about 10 or less. In yet another aspect of this invention, provided are reduced volatile organic solvent hair spray compositions having improved hair feel comprising silicone-containing hair setting polymer, an effective amount of an ionic strength modifier system for reducing viscosity of the compositions, as described above, and a liquid vehicle which comprises a mixture of water with one or more C₁-C₆ monohydric alcohols, wherein said composition comprises at least about 10 %, by weight, water.</p>					

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HAIR SPRAY COMPOSITIONS WITH IONIC STYLING POLYMER

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TECHNICAL FIELD

The present invention relates to hair spray compositions
10 which comprise a high molecular weight hair styling polymer. More particularly, this invention relates to hair spray compositions containing high molecular weight hair styling polymer and having improved sprayability.

BACKGROUND OF THE INVENTION

15 The desire to have the hair retain a particular shape is widely held. A common methodology for accomplishing this is applying hair styling, or hair "setting" compositions to the hair, typically to damp or dry hair. These compositions provide temporary setting benefits, and should be removable by water and/or
20 by shampooing. The materials used in the compositions to provide the setting benefits are generally applied in the form of mousses, gels, lotions or sprays.

25 High levels of style retention, or hold, are typically expected from hair styling compositions applied as a spray. Style retention is typically achieved by the use of resins, such as AMPHOMER, supplied by National Starch, and GANTREZ SP 225, supplied by GAF. As used in commercially sold hair spray products, these resins generally have a weight average molecular weight of from about 40,000 to about 150,000. When such resins are incorporated into pump and aerosol hair sprays, they can provide a combination of suitable style retention and good sprayability.
30 "Sprayability" refers to the spray quality and pattern. Good sprayability for hair spray formulations is characterized by a wide spray pattern without a wet, drippy center, and by sufficiently small droplet size to provide a fine mist.
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It remains desirable, however, to provide hair spray compositions that have improved hold and style retention performance. One technique for providing improved style retention for liquid hair spray compositions would be to utilize higher molecular weight hair styling resin. Alternately, this could reduce the amount of resin needed to provide a particular level of style retention. High molecular weight hair styling polymers, when utilized commercially, have typically been formulated as gels, lotions, or other non-spray compositions. Unfortunately, high molecular weight resins in liquid hair spray formulations tend to suffer from poor sprayability. More specifically, such formulations tend to have spray quality characterized by reduced spray pattern diameter, increased incidence of wet, drippy centers, and a tendency toward larger droplet size or streaming upon spraying, as opposed to a fine mist. This can result in overly heavy concentrations of hair spray in regions of the hair, causing the hair to be too stiff in those regions, whereas other areas may have too little hair spray applied and, consequently, have poor style retention and hold.

Thus, it is an object of this invention to provide liquid hair spray compositions utilizing high molecular weight styling resins that can provide improved style retention and retain good sprayability characteristics.

Recently, it has been found that certain polymers having silicone macromer portions can provide good style retention benefits to the hair while also providing improved hair feel. In other words, such silicone macromer-containing polymers can impart a tactile sense of softness and conditioning to the hair relative to conventional, non-silicone-containing resins. Silicone macromer-containing hair styling polymers and formulations containing them are disclosed, for example, in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al.,

- 3 -

issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319*, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320*, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

Whereas these silicone macromer-containing hair styling polymers can provide good overall hair styling performance with a desirable hair conditioning effect, they are preferably used in hair spray at relatively high molecular weights, compared to most commercial products (although they can also be used at more conventional hair spray resin molecular weights (e.g., about 50,000 to about 150,000 weight average molecular weight). Furthermore, they are difficult to formulate into a hair spray composition with good sprayability characteristics.

Therefore, it is another object of this invention to provide liquid hair spray compositions containing high molecular weight silicone-containing hair styling polymers which have improved spray characteristics.

It is also desirable to formulate hairspray compositions with reduced levels of volatile organic solvents, e.g., ethanol, propanol, etc. One way to do this is to increase the amount of water present in the composition at the expense of the volatile organic solvent. Unfortunately, this tends to adversely affect hairspray performance, especially drying time upon application, spray quality, and hair feel. This is particularly a problem for reduced volatile organic solvent compositions utilizing silicone macromer-containing hair setting resins. It is especially difficult to obtain good spray quality and hair feel from high water content compositions.

It is yet another object of this invention to obtain improved hairspray compositions containing silicone macromer-containing hair setting resins having reduced volatile organic solvents.

These and other objects as may be apparent to one skilled in the art can be obtained by the invention hereof, which is described in the description which follows. Unless otherwise in-

(*equivalent to EP 0412704 and 0412707, published 13 February 1991)

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dicated, all percentages and ratios herein are by weight.

SUMMARY OF THE INVENTION

The present invention provides improved sprayability hair spray compositions with high molecular weight hair styling polymers that can provide excellent hair styling/hold benefits upon spray application to the hair.

According to the present invention, sprayability of high molecular weight polymers can be improved through the use of ionic strength modifier systems consisting essentially of mixtures of non-surface active anions and cations. It is an essential aspect of the invention that the hair styling polymer also be of an ionic character.

More specifically, the present invention relates to a liquid hair styling composition useful for spray application to hair which comprises:

- (a) an ionic hair styling polymer having a weight average molecular weight of at least about 300,000;
- (b) a liquid vehicle selected from the group consisting of water, C₁-C₆, preferably C₂-C₄, monohydric alcohols, and mixtures thereof;
- (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of non-surface active cations and anions, wherein said cations and anions are at least partially soluble in said liquid carrier;

said composition having a pH of about 10 or less.

In one aspect of the invention, the high molecular weight hair styling polymer can be any of the conventional classes of hair styling or hair setting polymers in the art, i.e., polymers free of silicone portions.

In another aspect of the invention, the high molecular weight polymer is a silicone macromer-containing hair setting polymer that can provide hair styling and hold benefits while also providing improved softness to the hair relative to non-silicone-containing polymers. In yet another aspect of this

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invention, provided are reduced volatile organic solvent hairspray compositions having improved hair feel comprising silicone-containing hair setting polymer, an effective amount of an ionic strength modifier system for reducing viscosity of the compositions, as described above, and a liquid vehicle which comprises a mixture of water with one or more C₁-C₆, preferably C₂-C₄, monohydric alcohols, wherein said composition comprises at least about 10%, by weight, water.

DETAILED DESCRIPTION OF THE INVENTION

The essential as well as various optional components are described below.

Hair Styling Polymer

The compositions of the present invention contain an effective amount of a high molecular weight hair styling polymer to impart styling benefits upon application to hair. As used herein, "hair styling polymer" means any polymer, natural or synthetic, that can provide hair setting benefits. Polymers of this type are well known in the art. Generally, the level of hair styling polymer used will be at least about 0.1%, by weight, of the composition. Typically, it will be present at a level of from about 0.1% to about 15%, preferably from about 0.5% to about 8%.

The hair styling polymers hereof also are of ionic character. As used herein, "ionic hair styling polymer", or the term "ionic character" in reference to hair styling polymers or monomers of which such hair styling polymers are comprised, means hair styling polymers that are anionic, cationic, amphoteric, zwitterionic, or otherwise can exist in the liquid vehicle of the hair styling composition in dissociated form.

Any type of ionic hair styling polymer which is soluble or dispersible in the liquid carrier can be used in the present invention. A wide variety of such types of hair styling polymers are known in the art.

The ionic hair styling polymers hereof can be homopolymers, copolymers, terpolymers, etc. As used herein, the term "polymer" shall encompass all of such types of polymeric materials.

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As an essential aspect, the polymers hereof must comprise monomers of an ionic character. For convenience in describing the polymers hereof, monomeric units present in the polymers may be referred to as the monomers from which they can be derived. The 5 ionic monomers can be derived from polymerizable ionic starting monomers, or from polymerizable nonionic monomers which are modified subsequent to polymerization to be of ionic character. Also included are corresponding salts, acids and bases of the monomers exemplified.

10 Examples of anionic monomers include:

(i) unsaturated carboxylic acid monomers such as acrylic acid, methacrylic acid, maleic acid, maleic acid half ester, itaconic acid, fumaric acid, and crotonic acid;

15 (ii) half esters of an unsaturated polybasic acid anhydride such as succinic anhydride, phthalic anhydride or the like reacted with a hydroxyl group-containing acrylate and/or methacrylate such as hydroxyethyl acrylate and, hydroxyethyl methacrylate, hydroxypropyl acrylate and the like;

20 (iii) monomers having a sulfonic acid group such as styrene-sulfonic acid, sulfoethyl acrylate and methacrylate, and the like; and

(iv) monomers having a phosphoric acid group such as acid phosphooxyethyl acrylate and methacrylate, 3-chloro-2-acid phosphooxypropyl acrylate and methacrylate, and the like.

25 Examples of the cationic monomers include:

(i) monomers derived from acrylic acid or methacrylic acid, which is referred to hereinafter collectively as (meth)acrylic acid, and a quaternarized epihalohydrin product of a trialkylamine having 1 to 5 carbon atoms in the alkyl such as (meth)acryloyloxypropyltrimethylammonium chloride and (meth)acryloyloxypropyltriethylammonium bromide;

30 (ii) amine derivatives of (meth)acrylic acid or amine derivatives of (meth)acrylamide derived from (meth)acrylic acid or (meth)acrylamide and a dialkylalkanolamine having C₁-C₄ alkyl groups such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, or

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dimethylaminopropyl (meth)acrylamide; and

(iii) derivatives of the products of the group (ii) above by
(1) neutralization with an acid such as hydrochloric acid, or
lactic acid, (2) modification with a halogenated alkyl, such as
methyl chloride, ethyl chloride, methyl bromide, or ethyl iodide,
(3) modification with a halogenated fatty acid ester such as ethyl
monochloroacetate, or methyl monochloropropionate, and (4)
modification with a dialkyl sulfate such as dimethyl sulfate, or
diethyl sulfate.

10 Furthermore, the cationic unsaturated monomers include amine
derivatives of allyl compounds such as diallyldimethylammonium
chloride and the like.

15 These cationic unsaturated monomers can be polymerized in
cationic form, or as an alternative they can be polymerized in the
form of their precursors, which are then modified to be cationic,
for example, by a quaternizing agent (e.g. ethyl monochloro-
acetate, dimethyl sulfate, etc.).

20 Examples of the amphoteric monomers include zwitterionized
derivatives of the aforementioned amine derivatives of (meth)-
acrylic acids or the amine derivatives of (meth)acrylamide such as
dimethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acryl-
amide by a halogenated fatty acid salt such as potassium mono-
chloroacetate, sodium monobromopropionate, aminomethylpropanol
salt of monochloroacetic acid, triethanolamine salts of mono-
25 chloroacetic acid and the like; and amine derivatives of (meth)-
acrylic acid or (meth)acrylamide, as discussed above, modified
with propanesultone.

These amphoteric monomers, like the aforementioned cationic
monomers, can be polymerized in amphoteric form or, as an alterna-
30 tive, they can also be polymerized in the form of their pre-
ursors, which are then converted into the amphoteric state.

Preferred ionic monomers include acrylic acid, methacrylic
acid, dimethylaminoethyl methacrylate, quaternized dimethyl-
aminoethyl methacrylate, maleic acid, maleic anhydride half
35 esters, crotonic acid, itaconic acid, diallyldimethyl ammonium
chloride, polar vinyl heterocyclics such as vinyl imidazole, vinyl

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pyridine, styrene sulfonate, and mixtures thereof. Especially preferred ionic monomers include acrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, and mixtures thereof.

5 Salts of acid and amine monomers listed above can also be used, e.g., sodium, potassium, or other alkali or alkaline earth metal salts.

10 The polymers hereof should contain at least about 1%, by weight, ionic monomer, preferably at least about 2%, more preferably at least about 5%.

15 The hair styling polymers hereof can also contain nonionic monomers including, both high polarity monomers and low polarity monomers.

20 The ionic polymers hereof will generally comprise from about 1% to 100% ionic monomers and from 0% to about 99% nonionic monomers, preferably from about 2% to about 75% ionic monomers and from about 25% to about 98% nonionic monomers, more preferably from about 5% to about 50% ionic monomers and from about 50% to about 95% nonionic monomers.

25 Representative examples of low polarity nonionic monomers are acrylic or methacrylic acid esters of C₁-C₂₄ alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-24 carbon atoms with the average number of carbon atoms preferably being from about 4-18, more preferably from about 4-12; styrene; chlorostyrene; vinyl esters such as vinyl acetate; vinyl chloride; vinylidene chloride; acrylonitrile; alpha-methylstyrene; t-butyl-styrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; alkoxyalkyl (meth)acrylate, such as methoxy ethyl (meth)acrylate, butoxyethyl (meth)acrylate; and mixtures thereof. Other

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nonionic monomers include acrylate and methacrylate derivatives such as allyl acrylate and methacrylate, cyclohexyl acrylate and methacrylate, and methacrylate, oleyl acrylate and methacrylate, benzyl acrylate and methacrylate, tetrahydrofurfuryl acrylate and methacrylate, ethylene glycol di-acrylate and -methacrylate, 1,3-butyleneglycol di-acrylate and -methacrylate, diacetonacrylamide, isobornyl (meth)acrylate, and the like.

Preferred nonionic monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Representative polar nonionic monomers include acrylamide, N,N-dimethylacrylamide, methacrylamide, N-t-butyl acrylamide, methacrylonitrile, acrylamide, acrylate alcohols (e.g. C₂-C₆ acrylate alcohols such as hydroxyethyl acrylate and hydroxypropyl acrylate), methacrylate, and hydroxypropyl methacrylate, vinyl pyrrolidone, vinyl ethers, such as methyl vinyl ether, acyl lactones, vinyl pyridine, allyl alcohols, vinyl alcohols and vinyl caprolactam.

Examples of anionic hair spray polymers are copolymers of vinyl acetate and crotonic acid, terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate; and copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated aliphatic alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol; and acrylic copolymers and terpolymers containing acrylic acid or methacrylic acid as the anionic radical containing moiety such as copolymers with methacrylic acid, butyl acrylate, ethyl methacrylate, etc. Another example of an acrylic polymer which can be employed in the compositions of the present invention is a polymer of tertiary-butyl acrylamide, acrylic acid, and ethyl acrylate.

An example of an amphoteric polymer which can be used in the present invention is Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer, described generally in U.S. Pat. No.

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4,192,861 as being a polymer of N-tert-octyl acrylamide, methyl methacrylate, hydroxypropyl methacrylate, acrylic acid and t-butyl aminoethyl methacrylate, of appropriate molecular weight for purposes hereof.

5 Examples of cationic hair spray polymers are copolymers of amino-functional acrylate monomers such as lower alkylamino alkyl acrylate or methacrylate monomers such as dimethyl aminoethyl-methacrylate with compatible monomers such as N-vinylpyrrolidone or alkyl methacrylates such as methyl methacrylate and ethyl 10 methacrylate and alkyl acrylates such as methyl acrylate and butyl acrylate. Cationic polymers containing N-vinylpyrrolidone are commercially available from GAF Corp.

15 Still other organic, ionic hair styling polymers include carboxymethyl cellulose, copolymers of PVA and crotonic acid, copolymers of PVA and maleic anhydride, sodium polystyrene sulfonate, PVP/ethylmethacrylate/methacrylic acid terpolymer, vinyl acetate/crotonic acid/vinyl neodecanoate copolymer, octylacrylamide/acrylates copolymer, monoethyl ester of poly(methyl vinyl ether-maleic acid), and octylacrylamide/acrylate/butylaminoethyl 20 methacrylate copolymers. Mixtures of polymers may also be used.

Silicone-Containing Hair Styling Polymers

Preferred ionic hair styling polymers are silicone-containing polymers. Ionic silicone macromer-containing polymers are described, for example, in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319,* Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320,* Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

35 Examples of useful polymers and how they are made are also (*equivalent to EP 0412704 and 0412707, published 13 February 1991)

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described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference.

Preferred ionic silicone macromer-containing polymers comprise an organic polymeric backbone, preferably a vinyl backbone, having a Tg above about -20°C (more preferably above about 20°C) and, grafted to the backbone, a siloxane macromer having a weight average molecular weight of preferably at least about 500 preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000. In addition to the graft copolymers described above, silicone-containing polymers also include block copolymers preferably containing up to about 50% (more preferably from about 10% to about 40%) by weight of one or more siloxane blocks and one or more non-silicone blocks (such as acrylates or vinyls).

The silicone macromer-containing polymers preferred for use herein are such that when formulated into the finished hair care composition, and dried, the polymer phase separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the organic portion.

The silicone macromer-containing ionic hair styling polymers generally comprise nonionic silicone-containing monomers together with ionic monomers as described above, and can also contain non-silicone-containing nonionic monomers, also described above. The silicone-containing monomers also can be ionically charged and, as such, contribute, in part or in whole, to the overall charge density of the polymer.

The silicone-containing hair styling polymers hereof will generally comprise about 0.01% to about 50% of silicone-containing monomer, preferably from about 0.5% to about 40%, more preferably from about 2% to about 25%.

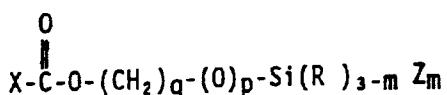
The silicone-containing monomer will generally have the formula:



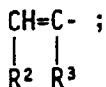
wherein X is a vinyl group copolymerizable with the other monomers

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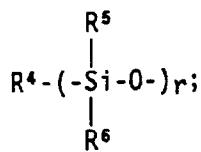
of the polymer; Y is a divalent linking group; R is a hydrogen, lower alkyl (eg. C₁-C₄), aryl, alkaryl, alkylamino, or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, and is pendant from the organic polymeric backbone; n is 0 or 1; and m is an integer from 1 to 3. Of course, Z should be essentially unreactive under polymerization conditions. The silicone-containing monomer preferably has a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably from about 5,000 to about 20,000. Preferably, it is of the formula:



wherein m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; X is



R² is hydrogen or -COOH (preferably R² is hydrogen); R³ is hydrogen, methyl or -CH₂COOH (preferably R³ is methyl); Z is



R³, R⁴, R⁵, R⁶ independently are alkyl, alkoxy, alkylamino, aryl, alkaryl, hydrogen, or hydroxyl (preferably alkyl, more preferably methyl); and r is an integer of at least about 10, preferably from about 5 to about 1500 (more preferably r is from about 75 to about 700, most preferably from about 100 to about 250. Particularly preferred are monomers when p=0 and q=3.

The silicone-containing monomers of the ionic polymers hereof can be polymerized in a silicone-containing monomer form. Alternatively, they can be polymerized in the form of their non-silicone containing precursor, and a silicone group can then be added. For example, carboxylate-containing monomers, such as acrylic

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acid, can be polymerized and then reacted with a silicone-containing compound with a terminal epoxy group. The result will, in general, be a silicone-containing monomer in the polymer having an equivalent structure to the formula $X(Y)_nSi(R)_{3-m}Z_m$, described above, and is intended to be encompassed herein.

The preferred silicone-containing polymers useful in the present invention generally comprise from 0% to about 98% (preferably from about 5% to about 98%, more preferably from about 50% to about 90%) of nonionic monomer, from 1% to about 98% (preferably from about 15% to about 80%) of ionic monomer, with from about 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of the monomers being silicone-containing monomer. The combination of the non-silicone-containing monomers preferably is from about 50% to about 99% (more preferably about 60% to about 99%, most preferably from about 75% to about 95%) of the polymer.

Exemplary silicone-containing polymers for use in the present invention include the following:

- (i) acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer-20,000 molecular weight
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate/PDMS macromer-20,000 molecular weight
- (iii)t-butylacrylate/acrylic acid/PDMS macromer-10,000 molecular weight
- (iv)t-butylacrylate/acrylic acid/PDMS macromer-10,000 molecular weight

The ionic hair styling polymers, including both silicone-containing and non-silicone containing polymers, having carboxylate or other acidic functionalities will preferably be utilized in at least partially neutralized form in the compositions hereof to promote solubility or dispersibility of the polymer in the vehicle. In addition, use of the neutralized form aids in shampoo removability of the hair spray compositions. In general, it is preferred that from about 10% to 100%, more preferably from about 20% to about 90%, even more preferably from

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about 40% to about 85%, of the acidic monomers of the polymer be neutralized.

Any conventionally used base, organic or metallic, may be used for neutralization of acidic polymers. Hydroxides of alkali metal and alkaline earth metal are suitable neutralizers for use in the present hair spray compositions. It will be recognized by those skilled in the art that various of the cations supplied neutralizing the polymer will also contribute to the ionic strength modifier system, as described herein.

Preferred neutralizing agents for use in hair spray compositions of the present invention are potassium hydroxide and sodium hydroxide.

Examples of other suitable neutralizing agents which may be included in the hair spray compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanol-amine (DIPA), triisopropanolamine (TIPA) and dimethyl steramine (DMS). Particularly useful for neutralization are mixtures of amines and metallic bases.

Polymers having basic functionalities, e.g., amino groups, are preferably at least partially neutralized with an acid, e.g., hydrogen chloride.

Liquid Vehicle

The hair spray compositions of the present invention also include a liquid vehicle. This can comprise any of those conventionally used in resin hair spray formulations. The liquid vehicle is present in the hair spray compositions at from about 80% to about 99%, preferably from about 85% to about 99%. More preferably, the liquid vehicle is present at from about 90% to about 98% of the total composition.

Organic solvents suitable for use in the liquid vehicle of the present compositions are C₁-C₆ alkanols, carbitol, acetone and mixtures thereof. C₁-C₆ alkanols preferred for use in the present

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compositions are C₂-C₄ monohydric alcohols such as ethanol, isopropanol and mixtures thereof. Water is also a preferred solvent for use in the liquid vehicle of the present hair spray compositions.

5 Preferably, the liquid vehicle for the present compositions is selected from the group consisting of C₁-C₆ alkanols, water, carbitol, acetone and mixtures thereof. More preferably, the liquid vehicle of the present composition is selected from the group consisting of water and C₂-C₄ monohydric alcohols such as ethanol and isopropanol, and mixtures thereof.

10 In general, water may be absent from the liquid vehicle or may comprise all of the liquid vehicle. Most preferably, the liquid vehicle is a mixture of water and organic solvents.

15 Where water and organic solvent mixtures are used, for instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the organic solvents are generally present in the range of from 0.5% to about 20 99%, preferably from about 50% to about 95%, by weight of the total composition.

25 In one aspect of the invention, the hair setting resin is of particularly high weight average molecular weight, i.e. weight average molecular weight above about 300,000, especially above about 500,000. It has been found that surprisingly effective hair spray performance can be obtained using these high molecular weight resins in combination with ionic strength modifier system. This invention is especially effective at providing the resins with characteristics in hair spray compositions such that they can 30 be sprayed with good spray quality, especially with respect to silicone macromer-containing hair setting resins, which are preferably used at relatively high molecular weights.

35 In another aspect of the invention, what is provided is a low volatile organic solvent hairspray composition which comprises a silicone macromer-containing ionic hair setting resin, an ionic strength modifier system as described herein, and a liquid

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vehicle. A reduced volatile organic solvent hair spray composition of the present invention comprises no more than 80% volatile organic solvents (which include, for purposes hereof, volatile silicone fluids and excludes water). In other embodiments hereof, 5 the hair spray compositions can comprise no more than about 65%, 55%, 50%, or other levels of volatile organic solvents, as may be chosen by product formulators. In the reduced volatile organic solvent hair spray products hereof, the hair spray compositions comprise at least 10%, by weight, of water. It is also specifically contemplated that they may contain at least about 10 11%, 12%, 13%, 14%, 15%, or more water. The weight average molecular weight of the silicone macromer-containing hair setting resins can be of any level suitable for providing effective hair styling. Typically, it will be at least about 50,000, more typically at least about 70,000, preferably at least about 15 100,000. As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In the more preferred embodiments of this aspect of the 20 invention, the weight average molecular weight of the resin is from about 70,000 to about 1,000,000, most preferably from about 100,000 to about 750,000.

In general, the reduced volatile organic solvent compositions 25 hereof will comprise up to about 90%, preferably up to about 70%, more preferably up to about 60%, even more preferably up to about 50% water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvents. It is also specifically contemplated that the compositions can be limited to no more than other maximum 30 limits on volatile organic solvents, e.g., no more than about 75%, 65%, or 55%, etc..

In general, for the compositions hereof, the weight average 35 molecular weight of the styling polymer is limited only by practical concerns. Generally, it will be below about 10,000,000, preferably below about 3,000,000, more preferably below about 1,000,000.

Ionic Strength Modifier System

The compositions of the present invention include, as an essential element, an effective amount of an ionic strength modifier system for reducing the viscosity of the hair styling composition, relative to the same composition absent the ionic strength modifiers. In general, the present compositions will comprise at least about 0.01%, by weight, of the ionic strength modifier. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the hair styling polymer will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, hair styling polymer, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched organic hetero-chain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus,

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basic and acidic ions OH⁻ and H⁺ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but they must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, e.g., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, e.g. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, amino-methylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions

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that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, e.g., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The compositions hereof have a water-equivalent pH of about 10 or less, preferably from about 3 to about 10, more preferably from about 5 to about 10. For purposes hereof, water-equivalent pH shall correspond to the pH of a composition containing all of the components of the composition, except that any non-aqueous component of the carrier is replaced by an equal weight of double reverse osmosis (DRO) water.

A preferred reduced volatile organic solvent hairspray composition of the present invention contains from about .01% to about 2% of a fluorosurfactant; from about 0.1% to about 15% of an ionic resin, including those having a weight average molecular weight of 300,000 and above, as well as those below 300,000, and also including those having silicone macromer portions as well as those without; an ionic strength modifier system as described herein, and a liquid vehicle comprising about 10% to about 45%, by weight of the composition water and about 50% to about 80%, by weight of the composition, of an organic solvent, preferably selected from the group consisting of ethanol, isopropanol and mixtures thereof.

The level of ionic strength modifier system used, in general, is given above. It is to be recognized, however, that the particular level of ionic strength modifier system which must be used to achieve an improvement in hair spray performance, or to achieve optimum performance, for a particular hair spray composition can vary depending upon a variety of factors, including the particular type of resin chosen and its molecular weight, and level in the composition, the specific ionic strength modifier system, the level of water and the type and level of volatile organic solvent, and the presence of optional components in the system. In gene-

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ral, higher levels of ionic strength modifier system may be needed to achieve a performance benefit as resin molecular weight and/or water levels are reduced. In general, the compositions hereof should contain at least an effective amount of the ionic strength modifier system provide an improvement in hair feel for a given level of hair hold performance or for improved spray quality (?).

Optional Ingredients

In addition to the ionic strength modifier system described above, the compositions hereof can optionally contain other materials to improve sprayability of the compositions. In particular, it is contemplated to utilize ionic surfactants in combination with the non-surface active anions and cations of the ionic strength modifier system hereof.

A wide variety of surfactants may be advantageously incorporated into the compositions hereof. These include anionic, cationic, amphoteric, and zwitterionic surfactants, and further include both fluorinated surfactants, as described below, and nonfluorinated surfactants.

Anionic surfactants include, for example: alkyl and alkenyl sulfates; alkyl and alkenyl ethoxylated sulfates; (preferably having an average degree of ethoxylation of 1 to 10), succinamate surfactants, such as alkylsulfosuccinamates and dialkyl esters of sulfosuccinic acid; neutralized fatty acid esters of isethionic acid; and alkyl and alkenyl sulfonates, including, for example, olefin sulfonates and beta-alkoxy alkane sulfonates. Preferred are alkyl and alkenyl sulfates and alkyl and alkenyl ethoxylated sulfates such as the sodium and ammonium salts of C₁₂-C₁₈ sulfates and ethoxylated sulfates with a degree of ethoxylation of from 1 to about 6, preferably from 1 to about 4, e.g., lauryl sulfate and laureth (3.0) sulfate.

Amphoteric surfactants include those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate,

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phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378. Others include alkyl, preferably C₆-C₂₂ and most preferably C₈-C₁₂, amphoglycinates; alkyl, preferably C₆-C₂₂ and most preferably C₈-C₁₂, amphopropionates; and mixtures thereof.

Suitable zwitterionic surfactants for use in the present compositions can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:

$$\begin{array}{c}
 (R^3)_x \\
 | \\
 R^2 --- Y(+) --- CH_2 --- R^4 --- Z(-) \\
 \end{array}$$

wherein R² contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R³ is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; x is 1 when Y is sulfur or phosphorus, 1 or 2 when Y is nitrogen; R⁴ is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups. Classes of zwitterionics include alkyl amino sulfonates, alkyl betaines, and alkyl amido betaines.

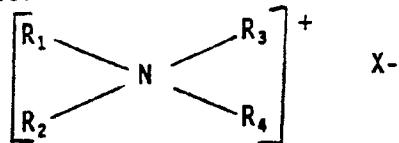
Cationic surfactants useful in compositions of the present invention contain amino or quaternary ammonium hydrophilic moi-

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eties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M. C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Pat. No. 3,155,591, Hilfer, issued Nov. 3, 1964; U.S. Pat. No. 3,929,678, Laughlin, et al., issued Dec. 30, 1975; U.S. Pat. No. 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Pat. No. 4,387,090, Bolich, Jr., issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:

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wherein R_1 is an aliphatic group of from 1 to 22 carbon atoms, or an aromatic, aryl or alkylaryl group having from 12 to 22 carbon atoms; R_2 is an aliphatic group having from 1 to 22 carbon atoms; R_3 and R_4 are each alkyl groups having from 1 to 3 carbon atoms, and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amido groups. Other quaternary ammonium salts useful herein are diquaternary ammonium salts.

Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein in the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid. (Tallow fatty acids give rise to quaternary compounds wherein R_1 and R_2 have predominately from 16 to 18 carbon atoms.)

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactants for use herein. The alkyl groups of such amines preferably have from 12 to 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl

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amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidyl-behenylamine. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Pat. No. 4,275,055, Nachtigal, et al., issued June 23, 1981 (incorporated by reference herein).

Suitable cationic surfactant salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts.

Nonionic surfactants can also be included in the compositions hereof. Preferably, the nonionic surfactants have an average HLB (Hydrophile-Lipophile Balance) of less than or equal to about 7.

Methods of determining HLB are well known in the art and any of such methods may be used for HLB determination. A description of the HLB System and methods for HLB determination are described in "The HLB System: a time saving guide to emulsifier selection," ICI Americas Inc.; Wilmington, Delaware; 1976.

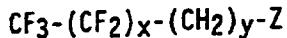
Nonionic surfactants include polyethylene oxide condensates of alkyl phenols (preferably C₆-C₁₂ alkyl, with a degree of ethoxylation of about 1 to about 6), condensation products of ethylene oxide with the reaction product of propylene oxide and ethylene diamine, condensation products of aliphatic alcohols with ethylene oxide, long chain (i.e., typically C₁₂-C₂₂) tertiary amine oxides, long chain tertiary phosphine oxides, dialkyl sulfoxides containing one long chain alkyl or hydroxy alkyl radical and one short chain (preferably C₁-C₃) radical, silicone copolyols, and C₁-C₄ alkanol amides of acids having a C₈-C₂₂ acyl moiety.

Fluorosurfactants (i.e., fluorinated surfactants) useful in the present compositions can be linear or branched alkyl, alkenyl or alkylaryl fluorohydrocarbons having a chain length of preferably 3 to 18 carbon atoms and being fully or partially fluorinated. The hydrophilic moiety can be, for example, sulfate,

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phosphate, phosphonate, sulfonate, amine, amine salts, quaternary ammonium, carboxylate, and any combination thereof. Also, there can be a bridging moiety between the hydrophilic and hydrophobic moieties, such as an amido alkylene group for example.

5 Ionic fluorosurfactants useful in the present compositions include perfluorinated compounds represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to 17, particularly from 7 to 11, and y is an integer from 0 to 4, and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, each being incorporated herein by reference.

20 Cationic fluorosurfactants preferred for use in the present compositions include fluorinated alkyl quaternary ammonium salts having a variety of anionic counter ions, including iodide, chloride, methosulfate, phosphate, and nitrate salts, preferably an iodide; and those fluorosurfactants conforming to the formula 25 $\text{RfCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3[\text{CH}_3\text{SO}_4]^-$ wherein $\text{Rf}=\text{F}(\text{CF}_2\text{CF}_2)_{3-8}$, such as ZONYL FSC supplied by E. I. DuPont deNemours and Company (Wilmington, Delaware, USA; DuPont). A preferred fluorinated alkyl quaternary ammonium iodide is FLUORAD FC-135 supplied by Minnesota Mining & Manufacturing (St. Paul, Minnesota, USA; 3M).

30 Anionic fluorosurfactants preferred for use in the present compositions are mono-, and bis-perfluoroalkyl phosphates, such as ZONYL FSP supplied by DuPont and conforming to the general formulae $(\text{RfCH}_2\text{CH}_2\text{O})\text{P}(\text{O})(\text{ONH}_4)_2(\text{RfCH}_2\text{CH}_2\text{O})_2\text{P}(\text{O})(\text{ONH}_4)$ wherein 35 $\text{Rf}=\text{F}(\text{CF}_2\text{CF}_2)_{3-8}$; mono- and bis-fluoroalkyl phosphates, having a

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variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, complexed with non-fluorinated quats, preferably aliphatic quaternary methosulfates, such as ZONYL FSJ supplied by DuPont; perfluoroalkyl sulfonic acid having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, such as ZONYL TBS supplied by DuPont and conforming to the formula $R_fCH_2CH_2SO_3X$ wherein $R_f=F(CF_2CF_2)_{3-8}$ and $X=H$ or NH_4 ; telomer phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably diethanolamine salts, such as ZONYL RP supplied by DuPont; amine perfluoroalkyl sulfonates, such as FLUORAD FC-99 supplied by 3M; ammonium perfluoroalkyl sulfonates, such as FLUORAD FC-93, FLUORAD FC-120 and L-12402, supplied by 3M; potassium perfluoroalkyl sulfonates, such as FLUORAD-95 and FLUORAD FC-98 supplied by 3M; potassium fluorinated alkyl carboxylates, such as FLUORAD FC-129 and FLUORAD FC-109 supplied by 3M; ammonium perfluoroalkyl carboxylates, such as Fluorad FC-143® supplied by 3M; and those fluorosurfactants conforming to the general formula $R_fCH_2CH_2SCH_2CH_2CO_2Li$ wherein $R_f=F(CF_2CF_2)_{3-8}$, such as ZONYL FSA supplied by DuPont.

Preferred anionic fluorosurfactants are mixed mono- and bis-perfluoroalkyl phosphates, ammonium salts; mixed mono- and bis-fluoroalkyl phosphate, ammonium salts, complexed with aliphatic quaternary methosulfates; perfluoroalkyl sulfonic acid, ammonium salts; mixed telomer phosphate diethanolamine salts; amine perfluoroalkyl sulfonates; ammonium perfluoroalkyl sulfonates; potassium perfluoroalkyl sulfonates; potassium fluorinated alkyl carboxylates; ammonium perfluoroalkyl sulfonates; and ammonium perfluoroalkyl carboxylates.

Amphoteric fluorosurfactants preferred for use in the present compositions are fluorinated alkyl amphoteric surfactants available commercially as FLUORAD FC-100 from 3M.

Zwitterionic fluorosurfactants preferred for use in the

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present compositions are those fluorosurfactants conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_{3-8}$ such as ZONYL FSK supplied by DuPont.

5 Preferably, mixtures of amphoteric or zwitterionic fluorosurfactants with anionic fluorosurfactants or mixtures of anionic and cationic fluorosurfactants are used.

The use of fluorosurfactants is especially desirable in reduced volatile organic solvent compositions, and most especially those with silicone macromer-containing polymers.

10 Surfactants are preferably included in the compositions at a level of from about 0.01% to about 2%, more preferably from about 0.01% to about 1.5%, most preferably from about 0.01% to about 1%.

Plasticizer

15 The performance of the hair styling polymers can be improved through the optional incorporation of a nonvolatile plasticizer into the composition. The plasticizer will generally be present in the compositions at a plasticizer: styling polymer weight ratio of about 1:20: to about 1:1, preferably from about 1:15 to about 20 1:2. As used herein, "nonvolatile" in regard to plasticizers means that the plasticizer exhibits essentially no vapor pressure at atmospheric pressure and 25°C. The polymer-liquid vehicle solution should not suffer from substantial plasticizer weight loss while the volatile carrier is evaporating, since this may 25 excessively reduce plasticization of the polymer during use. The plasticizers for use herein should generally have boiling points of about 250°C or higher.

Plasticizers are well known in the art and are generally described in Kirk-Othmer Encyclopedia of Chemical Technology, second edition, Volume 15, pp. 720-789 (John Wiley & Sons, Inc. 30 New York, 1968) under the topic heading "Plasticizers", and by J. Kern Sears and Joseph R. Darby in the text The Technology of Plasticizers (John Wiley & Sons, Inc., New York, 1982), both incorporated herein by reference. See especially in the Appendix 35 of Sears/Darby Table A.9 at pages 983-1063 where a wide variety of plasticizers are disclosed.

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Plasticizers include both cyclic and acyclic nonvolatile materials. Suitable categories of nonvolatile plasticizers include adipates, phthalates, isophthalates, azelates, stearates, citrates, trimellitates, silicone copolyols, iso C₁₄-C₂₂ alcohols, methyl alkyl silicones, carbonates, sebacates, isobutgrates, oleates, phosphates, myristates, ricinoleates, pelargonates, valerates, oleates, camphor, and castor oil, and silicone co-polyols.

Examples of adipate plasticizers include adipic acid derivatives such as diisobutyl adipate, bis(2-ethylhexyl) adipate, diisodecyl adipate, bis(2-butoxyethyl) adipate, and di-n-hexyl adipate.

Examples of phthalate plasticizers include phthalic acid derivatives such as dibutyl phthalate, butyl octyl phthalate, di-n-octyl phthalate, diisoctyl phthalate, bis(2-ethylhexyl) phthalate, n-octyl n-decyl phthalate, di-n-hexyl phthalate, isoctyl isodecyl phthalate, diisodecyl phthalate, ditridecyl phthalate, butyl cyclohexyl phthalate, butyl benzyl phthalate, dicyclohexyl phthalate, diphenyl phthalate, isodecyl benzyl phthalate, and bis(2-butoxyethyl) phthalate.

Isophthalate plasticizers include bis(2-ethylhexyl) isophthalate.

Examples of azelate plasticizers include azelaic acid derivatives such as di(2-ethylhexyl) azelate, and bis(2-ethylhexyl) azelate.

Examples of stearate plasticizers include stearic acid derivatives such as n-butyl stearate, butyl acetoxystearate, and butoxyethyl stearate.

Examples of citrate plasticizers include citric acid derivatives such as acetyl tri-n-butyl citrate, tri-n-butyl citrate, and acetyl tri-2-ethylhexyl citrate.

Examples of trimellitate plasticizers include tri-(2-ethylhexyl) trimellitate, and triisoctyl trimellitate.

Other examples of plasticizers include dibutyl carbonate, butyl oleate, n-butyl, butyrate, isobutyl butyrate, isopropyl

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5 butyrate, dibutyl carbonate, ethyl palmitate, isoctyl palmitate, methyl ricinoleate, butyl ricinoleate, diisooctyl sebacate, triisobutyl phosphate, isodecy pelargonate, ethyl valerate, isocetyl alcohol, octododecanol, isopropyl myristate, isostearyl alcohol and methyl alkyl silicones having C₂-C₂₀ alkyl and from 1 to about 500 siloxane monomer units, silicone copolyols, eg. dimethicone copolyol.

Hair Spray Compositions

10 Hair spray compositions of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

15 When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers.

20 Suitable propellants for use are volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas.

25 The hydrocarbons, particularly isobutane, used singly or admixed with other hydrocarbons are preferred.

30 The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 50% by weight of the total composition.

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Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from Americal National Can Corp.

5 Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON 10 AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other Ingredients

20 The hair spray formulations of the present invention can optionally contain a variety of other hair spray adjuvants as are known in the art. Generally, the compositions will comprise from about 0.05% to 5%, by weight, preferably from about 0.1% to 3%, by weight, of adjuvants. Hair spray adjuvants include: silicones; emollients; lubricants and penetrants such as various lanolin 25 compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints and other colorants; sunscreens; and perfume.

METHOD OF USE

30 The hair spray compositions of the present invention are used in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves spraying an effective amount of the product to dry or damp hair before or after the hair is styled, or both. By "effective amount" is meant an amount sufficient to provide the hair volume and style benefits 35 desired considering the length and texture of the hair.

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The following Examples illustrate the present invention. The Examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

5

EXAMPLES

Examples I-XVI

Hair spray compositions of the present invention are prepared according to the following formulations.

10

Example # (Weight Percent)

	<u>Ingredient</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>	<u>VII</u>	<u>VIII</u>
	Ethanol, 200 proof	79.3	79.3	79.2	79.2	79.1	79.1	79.2	79.2
	Isopropanol	--	10.4	10.4	10.4	10.4	10.4	10.4	10.4
	Hair Styling	4.0	2.6	2.6	2.6	2.6	2.6	2.6	2.6
15	Polymer ¹								
	KOH (45% aqueous solution) ²	0.82	0.7	0.8	0.8	0.8	0.8	0.8	0.8
	DRO Water ³	17.4	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	Potassium Chloride	0.02	0.05	0.02	-	-	-	-	-
20	Potassium Acetate	-	-	-	-	0.09	-	-	-
	Magnesium Acetate	-	-	-	-	-	-	-	-
	Acetic Acid	-	-	-	0.06	-	-	-	0.06
	Fluorosurfactant ⁴	-	-	-	-	-	0.1	0.05	-
	AMP ⁵	-	-	-	-	-			

25

Example # (Weight Percent)

	<u>Ingredient</u>	<u>IX</u>	<u>X</u>	<u>XI</u>	<u>XII</u>	<u>XIII</u>	<u>XIV</u>	<u>XV</u>	<u>XVI</u>
	Ethanol, 200 proof	79.2	86.6	86.3	43.3	86.6	80.0	75.9	75.8
	Isopropanol	10.4	10.4	10.4	10.4	10.4	10.4	-	-
	Hair Styling	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
30	Polymer ¹								
	KOH ²	0.8	-	-	-	-	-	3.3	3.3
	DRO Water ³	7.0	0.1	0.3	42.9	-	7.0	15.0	15.0
	Potassium Chloride	-	0.03	-	-	-	0.03	-	-
	Potassium Acetate	0.09	-	0.1	-	-	-	-	0.2
35	Magnesium Acetate	-	-	-	-	-	-	0.1	-
	Acetic Acid	-	-	-	0.5	-	-	-	-

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	Fluorosurfactant ⁴	-	-	-	-	0.05	-	-	-
	AMP ⁵	-	0.3	0.3	0.3	0.3	-	-	-

5 ¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone (PDMS) macromer - Example I, weight average molecular weight of about 150,000. Examples II-VI, weight average molecular weight of about 1.7 million; Examples VII-XIV, weight average molecular weight of about 800,000; Examples XV-XVI, weight average molecular weight of about 1.2 million.

10 ² Potassium hydroxide solution, containing 45% potassium hydroxide and 55% water and minors, except Examples XV and XVI, utilizing a 10% aqueous solution of potassium hydroxide.

15 ³ Double reverse osmosis water.

15 ⁴ ZONYL FSK containing 47% fluorosurfactant conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2(CH_2CO_2^-)$ wherein $R_f=F(CF_2CF_2)_{3-8}$ and 53% Acetic Acid and minors, supplied by E.I. DuPont de Nemours & Co., Inc. (Wilmington, Delaware, USA).

20 ⁵ 2-Amino-2-methyl-1-propanol.

20 The hair spray formulations are prepared by forming a premix of the polymer in isopropanol, and then adding the ethanol. For Examples I, XV and XVI, the polymer is added directly to the ethanol. A magnetic or air driven stirrer is used to mix the ingredients until the polymer is dissolved, typically about 1 to 2 hours. If used, the neutralizing agent (KOH or AMP, or both) is then added and mixed into the premix. Then, fluorosurfactant, any of the salts, and water, as may be applicable, are mixed into the composition.

30 Adjuvants may also be added to the compositions, including, for example, perfume or fragrance. The hair spray compositions prepared are especially suitable for pump spray application. The compositions will characterized by good sprayability characteristics and hair styling performance

Example XVII

35 A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

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	<u>Ingredient</u>	<u>Weight %</u>
	Ethanol, 200 proof	78.5
	Isopropanol	10.4
	Hair Styling Polymer ¹	2.6
5	KOH (45%)	0.7
	DRO Water	7.0
	FLUORAD FC-120 ²	0.4
	ZONYL FSK	0.5

10 ¹ 60% t-butyl acrylate/20% acrylate acid/20% PDMS macromer, having a weight average molecular weight of about 1,700,000.

2 ² FLUORAD FC-120 supplied by Minnesota Mining and Manufacturing Co. (3M), (St. Paul, Minnesota, USA) containing 25% ammonium perfluoroalkyl sulfonates, 37.5% ethanol and 37.5% water and minors.

15 Prepared as in Examples I-XVI.

Example XVIII

A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
20	Ethanol, 200 proof	89.1
	Hair Styling Polymer ¹	2.6
	KOH (45%)	0.7
	DRO Water	7.0
25	FLUORAD FC-120 ²	0.1
	ZONYL FSK	0.5

1 ¹ 60% t-butyl acrylate/20% acrylate acid/20% PDMS macromer, having a weight average molecular weight of about 1,700,000.

30 Prepared as in Examples I-XVI.

Example XIX

A hair spray composition of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
35	Ethanol, 200 proof	78.8

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	Isopropanol	10.4
	Hair Styling Polymer ¹	2.6
	KOH (45%)	0.8
	DRO Water	7.0
5	FLUORAD FC-120 ²	0.4
	ZONYL FSK	0.04

¹ 60% t-butyl acrylate/20% acrylic acid/20% PDMS macromer, having a weight average molecular weight of about 580,000.

10 Prepared as in Examples I-XVI.

Examples XX-XXII

A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

		Example XX	Example XXI	Example XXII
	<u>Ingredient</u>	(Wt %)	(Wt %)	(Wt %)
15	Ethanol, 200 proof	71.1	71.2	71.2
	Isopropanol	9.5	9.5	9.5
	Hair Styling Polymer ¹	2.4	2.4	2.4
20	KOH (45%)	0.6	0.6	0.6
	DRO Water	16.2	16.2	16.2
	ZONYL TBS ²	0.15	-	0.05
	ZONYL FSK	0.05	0.1	0.07

25 ¹ 60% t-butyl acrylate/20% acrylic acid/20% PDMS macromer, having a weight average molecular weight of about 800,000.

² ZONYL TBS, an anionic surfactant supplied by DuPont, containing 30-35% perfluoralkyl sulfonic acid ammonium salt, 2.4% acetic acid and 65%-70% water.

30 Prepared as in Examples I-XVI.

Examples XXIII-XXV

		Example XXIII	Example XXIV	Example XXV
	<u>Ingredient</u>	(Wt %)	(Wt %)	(Wt %)
35	Ethanol, 200 proof	78.9	79.4	78.2
	Isopropanol	10.4	10.4	11.2

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	Hair Styling Polymer ¹	2.6	2.6	2.8
	AMP	0.2	-	-
	KOH (45%)	0.6	0.4	0.5
	DRO Water	7.0	7.0	7.0
5	FLUORAD FC-120	0.1	0.1	0.2
	ZONYL FSK	0.05	0.05	0.09
	ZONYL TBS	0.07	-	-
	Fragrance	0.07	0.03	-

10 ¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer, having a weight average molecular weight of about 860,000 (Example XXIII), and 1.5 million (Example XXIV); and 1.7 million (Example XXV).

Prepared as in Examples IX-XVI.

EXAMPLE XXVI

15 A hair spray concentrate composition, of the present invention, which is suitable for aerosol dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
20	Ethanol, 200 proof	95.8
	Hair Styling Polymer ¹	3.0
	KOH	0.6
	AMP	0.4
	ZONYL FSK	0.25

25 ¹ 60% t-butyl acrylate/20% acrylic acid/20% silicone macromer, having average molecular weight of about 690,000.

30 ² ZONYL FSK supplied by DuPont, containing 40% mono- and bis-fluoroalkyl phosphates, ammonium salt, complexed with aliphatic quaternary methosulfate, 15% isopropyl alcohol and 40-45% water.

35 Prepared as in Examples I-XVI. The concentrate is packaged in a conventional aerosol spray can and charged with a conventional liquifiable propellant at a propellant:concentrate weight ratio of 30:70.

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Examples XXVII-XXX

	<u>Ingredient (wt.%)</u>	<u>XXVII</u>	<u>XXVIII</u>	<u>XXIX</u>	<u>XXX</u>
5	Ethanol, 200 proof	79.3	80.1	79.3	79.5
	Isopropanol	10.4	10.4	10.4	10.4
	Hair Styling Polymer ¹	2.6	-	-	-
	Hair Styling Polymer ²	-	1.8	-	-
10	Hair Styling Polymer ³	-	-	2.0	-
	Hair Styling Polymer ⁴	-	-	-	1.8
	KOH (10% aqueous solution)	-	-	1.2	1.2
	HCl (10% aqueous solution)	0.6	0.6	-	-
15	DRO Water	7.0	7.0	7.0	7.0
	Potassium Chloride	0.10	0.10	0.10	0.10
	¹ 15% t-butylaminoethylmethacrylate/15% t-butylacrylamide/70% ethylmethacrylate, having a weight average molecular weight of about 1.2 million.				
	² 15% t-butylaminoethylmethacrylate/15% t-butylacrylamide/60% ethylmethacrylate/10% PDMS macromer (weight average molecular weight of about 10,000), having a weight average molecular weight of about 1.2 million.				
20	³ 15% N,N dimethylacrylamide/70% isobutylmethacrylate/15% acrylic acid, having a weight average molecular weight of about 1.2 million.				
	⁴ 15% N,N dimethylacrylamide/60% isobutylmethacrylate/15% acrylic acid/10% PDMS macromer (weight average molecular weight of about 10,000), having a weight average molecular weight of about 1.2 million).				
	Prepared as in Examples I-XVI, except for Examples XXVII and XXVIII, the HCl is added as the neutralizer.				
	The above compositions will exhibit good sprayability and when applied to the hair, provide good hair styling benefits.				
30	In the above examples and the compositions hereof utilizing silicone macromer-grafted styling resins, it can be desirable to purify the styling resin by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at				
35					

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25°C of about 10,000,000 centistokes and less. This can be done, for the example, by hexane extraction. After drying the resin from its reaction solvent hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Low molecular weight polysiloxane-containing monomer and polymer about 1 hour is solubilized by the supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurized and dry, extracted polymer is recovered from the extraction vessel.

In the above examples and the compositions hereof utilizing silicone macromer-grafted styling resins, the resin can be purified by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for the example, by hexane extraction. After drying the resin from its reaction solvent, hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

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CLAIMS:

1. A liquid hair styling composition useful for spray application to hair, said composition characterized in that it comprises:
 - (a) an ionic hair styling polymer having a weight average molecular weight of at least 300,000;
 - (b) a liquid vehicle selected from the group consisting of water, C₁-C₆ monohydric alcohols, and mixtures thereof;
 - (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle;
said composition having a pH of 10 or less.
2. A liquid hair styling composition as in Claim 1, comprising from 0.1% to 15%, by weight, of said ionic hair styling polymer, from 80% to 99.5%, by weight, of said liquid vehicle, and from 0.01% to 4%, by weight of said ionic strength modifier system.
3. A liquid hair styling composition as in Claim 1 or 2, wherein said ionic hair styling polymer comprises from 2% to 75% ionic monomers, and from 25% to 98% nonionic monomers.
4. A liquid hair styling composition useful for spray application to hair, said composition characterized in that it comprises:
 - (a) an ionic hair styling polymer having a weight average molecular weight of at least 300,000; said ionic hair styling polymer comprising silicone-containing monomers, wherein when the composition is dried, the hair styling polymer separates into a discontinuous phase

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which includes the silicone portion of said polymer and a continuous phase which includes the non-silicone portion;

- (b) a liquid vehicle selected from the group consisting of water, C₂-C₄ monohydric alcohols, and mixtures thereof;
- (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle; said composition having a pH of 10 or less.

5. A liquid hair styling composition as in Claim 4, wherein said polymer comprises at least 0.5% of silicone macromer-containing monomers.

6. A liquid hair styling composition as in Claim 4 or 5, comprising from 5% to 95% of ionic monomers and from 5% to 95% of nonionic monomers.

7. A liquid hair styling composition as in Claim 1, 2, 3, 4, 5, or 6, wherein said cations are sodium, potassium, magnesium, or a mixture thereof, and said anions are sulfate, acetate, chloride, or a mixture thereof.

8. A liquid hair styling composition as in Claim 1, 2, 3, 4, 5, 6, or 7, wherein said ionic hair styling polymer has a weight average molecular weight of at least 500,000.

9. A liquid hair spray composition as in Claim 3 or 6, wherein said ionic monomer is acrylic acid, methacrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl

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methacrylate, maleic acid, half esters of maleic anhydride, crotonic acid, itaconic acid, diallyldimethyl ammonium chloride, vinyl pyridine, vinyl imidazole, styrene sulfonate, or a mixture thereof, and said nonionic monomer is selected from the group consisting of acrylic acid esters of C₁-C₂₄ alcohols, methacrylic acid esters of C₁-C₂₄ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alphamethylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof.

10. A liquid hairspray product comprising a hairspray composition and a spray dispenser means for containing and spraying said composition, said composition being contained in said spray dispenser means, said hairspray composition characterized in that it comprises:

- (a) an ionic, silicone macromer-containing hair styling polymer;
- (b) a liquid vehicle selected from the group consisting of water, C₁-C₆ monohydric alcohols, and mixtures thereof,
- (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle;

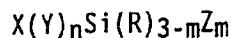
said composition having a pH of 10 or less and comprising from 10% to 90%, by weight, water, and from 10% to 80%, by weight, of said monohydric alcohols.

11. A liquid hairspray product as in Claim 10, comprising from 0.1% to 15%, by weight, of said hair styling polymer, from 80% to 99.5%, by weight, of said liquid vehicle selected from the group consisting of C₂-C₄ monohydric alcohols and water, and from 0.01% to 4%, by weight, of said ionic strength modifier system.

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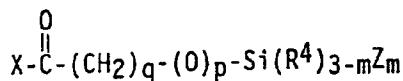
12. A liquid hairspray product as in Claim 10 or 11, wherein said cations are sodium, potassium, magnesium, or a mixture thereof, and said anions are sulfate, acetate, chloride, or a mixture thereof.

13. A liquid hair styling composition or product as in Claim 4, 5, 6, 10, 11, or 12, wherein said silicone macromer-containing monomers have the formula:



wherein X is a vinyl group; Y is a divalent linking group; R is a hydrogen, lower alkyl, aryl or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500; n is 0 or 1; and m is an integer from 1 to 3.

14. A liquid hair spray composition or product as in Claim 13, wherein said silicone macromer-containing monomer is:

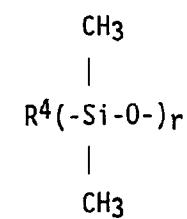


wherein m is 1, 2, or 3, p is 0 or 1, q is an integer from 2 to 6,

X is $CH=C-$



R¹ is -H or -COOH, R² is -H, -CH₃, or CH₂ COOH, R⁴ is alkyl, alkoxy, alkylamino, aryl or hydroxyl, and Z is



wherein r is an integer from 5 to 700.

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15. A liquid hair spray product as in any of Claims 10-14, wherein said polymer comprises at least 0.5% of silicone macromer-containing monomers.

16. A liquid hair spray product as in any of Claims 10-15, comprising from 5% to 95% of ionic monomers and from 5% to 95% of nonionic monomers.

17. A liquid hair spray composition or product as in Claim 16, wherein said ionic monomer is acrylic acid, methacrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, maleic acid, half esters of maleic anhydride, crotonic acid, itaconic acid, diallyldimethyl ammonium chloride, vinyl pyridine, vinyl imidazole, styrene sulfonate, or a mixture thereof.

18. A liquid hair spray composition or product as in Claim 17, wherein said polymer comprises 15% to 80% of said ionic monomer, 50% to 90% of nonionic monomer selected from the group consisting of acrylic acid esters of C₁-C₂₄ alcohols, methacrylic acid esters of C₁-C₂₄ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alphamethylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof and 2% to 25% of said silicone-containing monomer.

19. A method for providing hair setting benefits to the hair, comprising spraying an effective amount of any of the compositions of Claims 1-18 to hair.

INTERNATIONAL SEARCH REPORT

PCT/US 92/06975

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.C1. 5 A61K7/06; A61K7/11

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.C1. 5	A61K

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ^a	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 412 704 (THE PROCTER & GAMBLE COMPANY) 13 February 1991 cited in the application see the whole document	1-19
X	EP,A,0 412 707 (THE PROCTER & GAMBLE COMPANY) 13 February 1991 cited in the application see the whole document	1-19
X	EP,A,0 412 710 (THE PROCTER & GAMBLE COMPANY) 13 February 1991 cited in the application & US,A,5 106 609 see the whole document	1-19

^a Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

18 DECEMBER 1992

Date of Mailing of this International Search Report

30.12.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

GAC G.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP,A,0 408 311 (MITSUBISHI PETROCHEMICAL COMPANY LIMITED) 16 January 1991 cited in the application see the whole document ---	1-19
X	EP,A,0 101 920 (KAO CORPORATION) 7 March 1984 see the whole document ---	1-3,7-9
X	US,A,3 958 581 (J.L. ABEGG ET AL.) 25 May 1976 see the whole document ---	1-3,7-9
X	EP,A,0 059 428 (KAO SOAP COMPANY LTD) 8 September 1982 see the whole document ---	1,2,7,8, 19
X	LU,A,65 373 (L'OREAL) 23 November 1973 see the whole document ---	1,2,7,8, 19
X	EP,A,0 370 338 (NATIONAL STARCH AND CHEMICAL CORPORATION) 30 May 1990 see the whole document ---	1,2,7,8
X	GB,A,2 098 226 (L'OREAL) 17 November 1982 see the whole document -----	1,2,7,8
A	---	3,9
X	FR,A,2 355 497 (UNILEVER N.V.) 20 January 1978 see the whole document -----	1,2,19

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9206975
SA 64051

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date		Patent family member(s)	Publication date
EP-A-0412704	13-02-91		AU-B- 624014 AU-A- 6015890 CA-A- 2022467 CN-A- 1049784 JP-A- 3128311	28-05-92 07-02-91 08-02-91 13-03-91 31-05-91
EP-A-0412707	13-02-91		AU-A- 6015690 CA-A- 2022466 CN-A- 1049786 JP-A- 3128312	07-02-91 08-02-91 13-03-91 31-05-91
EP-A-0412710	13-02-91		US-A- 5106609 AU-A- 6015990 JP-A- 3218306 CN-A- 1056051	21-04-92 07-02-91 25-09-91 13-11-91
EP-A-0408311	16-01-91		JP-A- 3128909	31-05-91
EP-A-0101920	07-03-84		JP-C- 1343493 JP-A- 59020396 JP-B- 61010517 CA-A- 1212297 GB-A,B 2124245 US-A- 4534892	29-10-86 02-02-84 29-03-86 07-10-86 15-02-84 13-08-85
US-A-3958581	25-05-76		AT-B- 332561 AU-A- 5585373 BE-A- 799545 CA-A- 1001076 CH-A- 572336 DE-A,B,C 2324797 FR-A,B 2184890 GB-A- 1401089 LU-A- 65373 NL-A- 7306769 SE-B- 422408	11-10-76 21-11-74 16-11-73 07-12-76 13-02-76 29-11-73 28-12-73 16-07-75 23-11-73 20-11-73 08-03-82
EP-A-0059428	08-09-82		JP-A- 57144213 JP-B- 61060805 US-A- 4895722	06-09-82 23-12-86 23-01-90

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9206975
SA 64051

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 18/12/92
Page 2

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
LU-A-65373	23-11-73	AT-B- AU-A- BE-A- CA-A- CH-A- DE-A, B, C FR-A, B GB-A- NL-A- SE-B- US-A-	332561 5585373 799545 1001076 572336 2324797 2184890 1401089 7306769 422408 3958581	11-10-76 21-11-74 16-11-73 07-12-76 13-02-76 29-11-73 28-12-73 16-07-75 20-11-73 08-03-82 25-05-76
EP-A-0370338	30-05-90	US-A- AU-B- AU-A- CA-A- DE-U- JP-A-	4996045 628094 4390389 2001977 6890160 2196710	26-02-91 10-09-92 07-02-91 16-05-90 25-06-92 03-08-90
GB-A-2098226	17-11-82	LU-A- BE-A- CA-A- CH-A- DE-A- FR-A, B JP-B- JP-A- NL-A- SE-A- US-A-	83350 893113 1179268 652920 3216687 2505179 4000961 57198800 8201877 8202843 4842849	24-03-83 08-11-82 11-12-84 13-12-85 02-12-82 12-11-82 09-01-92 06-12-82 01-12-82 09-11-82 27-06-89
FR-A-2355497	20-01-78	GB-A- AT-B- AU-B- AU-A- BE-A- CA-A- CH-A- DE-A, B JP-C-	1584364 376566 513953 2621777 855845 1088867 627643 2727255 1555440	11-02-81 10-12-84 15-01-81 04-01-79 19-12-77 04-11-80 29-01-82 29-12-77 23-04-90

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9206975
SA 64051**

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The members are as contained in the European Patent Office EDP file on
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Page 3

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2355497		JP-A- 52155608	24-12-77
		JP-B- 60017768	07-05-85
		NL-A- 7706750	23-12-77
		SE-B- 434118	09-07-84
		SE-A- 7707128	22-12-77
		US-A- 4272515	09-06-81